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DIELECTRIC COMPOSITE THIN FILMS

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Mixed composition films are widely used in gradient index and in discrete optical coatings. This study addressed the composition dependent properties of these films with special emphasis on the effect of composition on the film microstructure and structure-property relationships

One visible, TiO_2-SiO_2, and two potential infrared, $ZnSe$-SrF_2 and Si-YF_3, material systems were studied. The effect of composition, deposition and post-deposition treatment conditions on film properties such as intrinsic stress, moisture penetration, refractive index, optical scatter, morphology and crystallization have been investigated.

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The macroscopic film properties were observed to strongly depend on composition. This is not only due to averaging of the properties of the pure constituents in the mixture but also because of unique film microstructures engendered by the composite chemical environment during film growth. In general many of the microstructure dependent properties (e.g., stress) vary nonlinearly with composition and cannot be predicted on the basis of the properties of the pure constituents.

In this study the process conditions and compositions that produce films with low stress, smooth morphology, dense microstructure and low or no water content have been established in the three material systems studied. (AW)

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FOREWORD

The goals of this project were the investigation of the effects of composition on the properties of evaporated composite dielectric thin films and analysis of structure-property relationships in these films.

The composition and microstructure dependent properties of three binary material systems have been studied. In the first part of the project, the TiO_2-SiO_2 composite system, which is a widely used combination in gradient index optical coatings, was investigated in detail. Thin film properties such as intrinsic stress, moisture content, crystallization and interdiffusion have been analyzed as functions of deposition and annealing conditions and composition. A model relating these macroscopic properties to the film microstructure and its chemical composition has been developed.

In the second part, two binary systems, $ZnSe$-SrF_2 and YF_3-Si, that are useful IR material combinations, were studied with special emphasis on film microstructure. Intrinsic stress, optical scatter, crystallinity and surface morphology, and their dependences on composition and post deposition annealing were investigated.

These studies have determined compositions, and deposition and annealing conditions that produce environmentally stable thin films with low stress, smooth surface morphology, little or no moisture penetration, and low optical scatter. The trends indicated by the dependences of properties on preparation conditions, and models that explain them in terms of the film microstructure, should also be applicable to other dielectric material systems.

The results of this study are presented in detail in the appendices and also summarized in the body of the report. Relevance of these results to improvement of optical coatings is also discussed.

1.0 INTRODUCTION

1.1   Tehnical Background

Dielectric mixtures are widely used in gradient index, as well as in discrete index coatings, to attain desired optical constants (refractive index and extinction coefficient). The optical constants generally scale with film composition and therefore any arbitrary value between the values of the pure materials can be obtained for the mixed composition films by simply adjusting the evaporation rates of the pure constituents. One type of gradient index coating that has recently received wide attention is the rugate filter, where the refractive index, and hence composition, in the film growth direction varies sinusoidally. In contrast to optical constants, many of the structure dependent properties such as stress, optical scatter etc. generally do not depend linearly on composition. These nonoptical properties are also of primary importance for the performance and reliability of the optical coatings. In this study we have emphasized these structure and composition dependent properties in three binary material systems.

This project was also carried out in conjunction with Air Force funded rugate programs. The in-depth material studies of this program complemented the device oriented studies of the rugate programs. The rugate programs have broad scopes and focus on feasibility, design, materials, fabrication and characterization aspects of rugate technology. In the "Dielectric Alloy" program we have studied one material system that is currently used for rugates, and two other potentially useful rugate material systems. The constituents of these composite systems, TiO_2-SiO_2 for the visible range and Si-YF_3 and ZnSe-SrF_2 for the infrared range, are commonly used materials in the optical coating industry. The results of this study are not necessarily specific to the above material systems but have broad implications for dielectric coatings of mixed or discrete compositions of other materials.

1.2   Properties of Thin Films

Film properties can vary widely depending on the deposition technique, deposition conditions and material purity and film composition. Deposition technique and conditions affect the chemical (state of dissociation or excitation) and kinetic (velocity of the vapor species) energies of the evaporants. These energies in turn affect the film

microstructure by determining the extent of surface atom migration, i.e., adatom mobility, and the chemical reactivity of these species.

Temperature, deposition pressure and rate are the only parameters that can be controlled in conventional deposition techniques. Generally, higher temperatures and lower pressures generate a higher packing density and smaller porosity, and therefore fewer paths for moisture penetration and smaller surface area for water adsorption, than low temperature or high pressure conditions.

The high gas pressures ($1-2 \times 10^{-4}$ Torr), often required to form stoichiometric films in oxide based materials, lead to low packing density. This is due to the energy loss of the evaporants via collisions with the reactive gas molecules (e.g., O_2) during their transit from the evaporation source to the substrate. This fact is not widely recognized but accounts for the low refractive index and moisture in dielectric films of many compounds. The physical cause for the low packing density, collisions with the background gas particles, has been unequivocally demonstrated in our work (Appendix 1).

Film composition, including impurities, can also affect the microstructure by altering the chemical environment of the condensing atoms, the surface energy of the grains, and possibly the adatom mobility of the species during deposition.

The film microstructure and the chemistry of the grains strongly affect many macroscopic film properties, e.g., stress. In mixed composition films, microstructure dependent properties are often observed to vary nonlinearly with composition. Therefore a detailed understanding of the film microstructure and its relationship to the film properties are essential in explaining and predicting the dependence of the film properties on deposition conditions and its chemical composition.

As an example, the effect of the microstructure on the intrinsic stress can be understood in terms of the intergrain forces within the film. In a polycrystalline or grainy dielectric coating, the extent of porosity and the grain size affect the number of grain interfaces and their separation as well as the strain in the bonds across these grains. The composition determines the density of dangling bonds, the nature of the surface chemistry, and the propensity of the surfaces to adsorb species (e.g., water) from the environment, and even the particular bonding arrangement of the adsorbed species on the surfaces. All of the above will influence the type (attractive vs repulsive) and the magnitude of the intergrain forces within the film and its macroscopic manifestation, the

intrinsic stress. For the above reasons we have emphasized microstructure studies of the films under study, with experiments directed toward uncovering microstructure-macroscopic property relationships.

2.0 SUMMARY OF RESULTS

In this section we briefly summarize the results that are discussed in full detail in the publications (see Appendices) and discuss observations and data that are not included in the publications although being relevant to rugate programs. The TiO_2-SiO_2 system will be discussed first with special emphasis on stress and stress related failure, water, the effect of annealing on water content and on crystallization. In the subsequent section, the composition and microstructure dependent properties of ZnSe-SrF_2 and Si-YF_3 systems will be discussed.

2.1 TiO_2-SiO_2 Visible Composite System

TiO_2 and SiO_2 are commonly used optical materials both in discrete and in mixed composition coatings. Some of the reasons for their desirability are the large refractive index difference, formation of hard coatings and absence of intermediate compounds or phases. The materials have elevated melting temperatures, are immiscible but form homogeneous films in mixed composition films under all deposition conditions of practical interest. This is due to low surface mobility of the adatoms during deposition, causing the vapor phase composition to "freeze" upon condensation.

The low surface adatom mobility, due to relatively low deposition temperatures (roughly 25% of the melting point), also causes formation of columnar grains and a void network in the film microstructure, as expected from the well known Movchin-Demyishin model.[1]

2.1.1 Stress and Stress Induced Failure

TiO_2 and composite TiO_2-SiO_2 films, of the considerable thicknesses that are encountered in rugate filters, are often observed to mechanically fail by cracking and peeling. These stress induced failures are also observed to be sensitive to environment, occurring either after exposure to ambient air after deposition, or exposure to vacuum following exposure to air. These observations suggest that sorbed water plays an important role in the stress behaviour of these films.

As shown in Figs. 1 and 2, stress causes cracks to form in the film-substrate surface and causes the substrate surface to fracture and peel. These indicate that the

interfacial adhesion strength of the rugate coating to the substrate is larger than fracture strength of the glass substrate. Microscopic inspection of the crack formation indicated that the cracks propagate between the nodules, the latter apparently acting as stress concentrators. Figure 2 shows that the film has separated from the nodule. This condition will cause large stresses in the hoop direction. The observed stress induced failure of these films fits one of the thin film-substrate behaviour modes under stress, corresponding to the case of hard substrate and hard film with good adhesion.[2]

Ambient water plays a significant role in the stress-induced failure of these films by exacerbating the stress and probably by lowering the fracture strength of the material, as explained below. Water, and to a lesser extent other polar adsorbates, are known for their strong propensity to hydrolyze on the surfaces of silicates and other metal oxides.[3] This tendency is enhanced at the stress zones due to larger energy gain in the hydrolysis of strained or dangling bonds. Formation of hydroxide groups leads to breaking of the structural Si-O or Ti-O bonds and to exposing the bonds underneath the surface to attack by water. This stressed area or crack tip propagates, bond by broken bond, into the material lowering its fracture strength.[4]

The effect of sorbed water on stress is very pronounced as seen in Fig. 3. This figure shows the stress behaviour of a film of composition of 30% TiO_2-70% SiO_2, as it is treated in different environments. The film has moderate compressive stress in air after a 350°C annealing step. Exposure to vacuum and subsequent baking causes water desorption and a large increase in tensile stress. This suggests that thick films formed under these conditions may fail in a space environment as water absorbed in the earth environment is desorbed in space.[5]

Following water desorption, any stress effect due to thermal cycling in vacuum is due to the thermal expansion coefficient difference between the film and the substrate. This is seen to be small in comparison to stress excursions due to water sorption-desorption. Exposure to ambient air restores the original stress level. However this restoration occurs with two distinct temporal behaviours, one with a time constant of seconds, and a slower one with a time constant that varies from hours to days, depending on the preparation conditions. These two time constants may indicate the existence of two types of absorption sites, possibly grain surfaces and intragrain pores.

Fig. 1

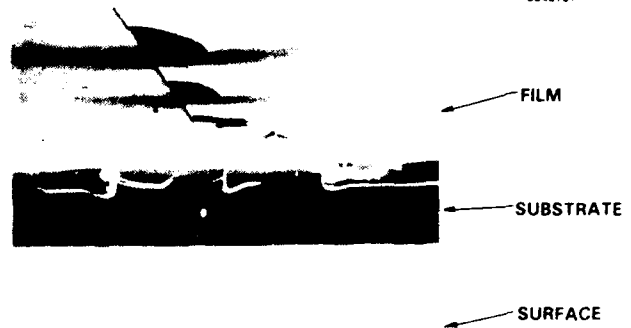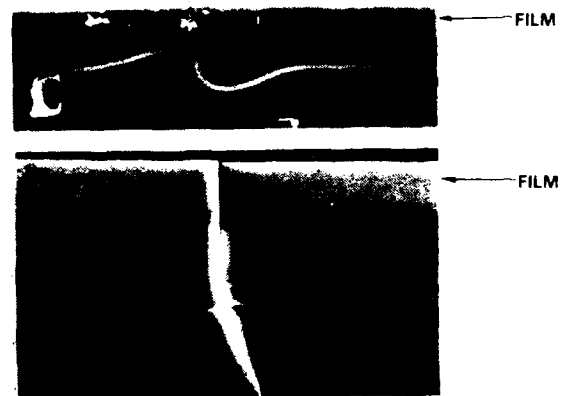Morphology of stress induced fracture
in composite TiO_2-SiO_2 films on
glass substrate.

FILM

SUBSTRATE

SURFACE

FILM

FILM

Fig. 2

SEM micrographs of nodules and cracks.

BANDS
IN THE
FILM

NODULE NEST

SUBSTRATE

DELAMINATION
IN THE
SUBSTRATE

STRESS BEHAVIOR OF A SiO₂·TiO₂
MIXED COMPOSITION FILM
DEPOSITION PRESSURE = 1x10⁻⁴ TORR O₂
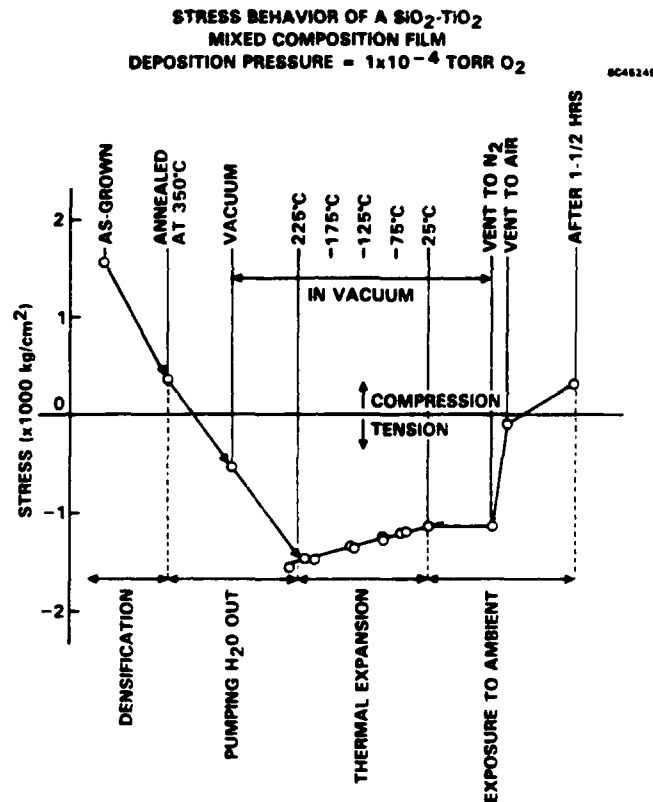
Fig. 3   Stress behavior of a composite TiO_2-SiO_2 film in various
environments.

In the above example, the silica rich films, prepared under the indicated conditions, exhibited compressive stress due to water sorption. Mixed composition films, prepared under different conditions, and especially TiO_2 rich films exhibit tensile stress due to water sorption. In our structure-property model this difference in behaviour is attributed to different arrangement of the water (OH-) molecules on the grain surfaces. SiO_2 films are more tightly packed but also adsorb more water. Large numbers of OH-molecules, tightly packed on the grain surfaces of small porosity material, could be forced to form sheets of dipoles. This will cause repulsive forces across the grains, leading to compressive stress. TiO_2 rich films are less tightly packed but also adsorb less water, allowing OH-s more freedom to arrange causing them to form hydrogen or hydroxil bonds across the grains which increase the attractive forces between the grains, leading to tensile stress. To investigate the validity of this plausible hypothesis, we investigated the IR spectrum of the films. These show a broad absorption peak due to

the OH stretch band, suggesting the coexistence of different bonding arrangements but making it impossible to resolve a dominant mode in any of the films. The larger sorptivity of SiO_2 films for water than TiO_2 films is probably structure dependent although differences in coordination of the atoms can also account for the observed difference. Elements with fewer bonds (Si is 4-fold and Ti is 6-fold) will undergo more severe distortion as a result of a dangling bond and therefore will tend to bond more readily to adsorbates to satisfy the dangling bonds and to lower their energies.

The details of the dependence of stress on deposition conditions are shown in the figures in the paper reprinted in this report titled "Sorbed Water and Intrinsic Stress in Composite TiO_2-SiO_2 Thin Films." As expected from the above arguments, the stress becomes less tensile or more compressive under deposition conditions, such as high temperature, low pressure or energetic ion bombardment, that produce a more densely packed structure.

The composition dependence of intrinsic stress shows nonlinear behaviour in codeposited (analog) and linear behaviour in layered (digital) films. The nonlinear behaviour observed in codeposited films had also been seen in mixtures of Ge with ZnSe, CdTe, MgF_2 and CeF_3 [6] as well in the IR systems investigated under this program, ZnSe-SrF_2 and YF_3-Si. The nonlinear behaviour of the analog films is due to the fact that the microstructure, that strongly affects stress, does not vary linearly with composition. Factors such as bond strengths, chemical environment of the atoms and of the grains, surface mobility of the species during deposition that affect bonding, and both short and long range order can induce a microstructure that is unique to the mixed composition film.

2.1.2   Water in the Films and Effects of Annealing

Moisture in the films was observed to depend on the initial film porosity and silica content. Thus, films formed at high temperatures and low pressures, as well as under ion bombardment during deposition, have higher packing density and lower water content, than films formed under opposite conditions. Evidence for the porous and granular nature of the films deposited at high gas pressures can be obtained, in situ, by ellipsometry.

Reflection of light will be sensitive to the polarization direction (s or p) and to the microstructure (column shape and size) due to form birefringence. Ellipsometry measures the reflectances for both polarization states. A visually discriminating method of displaying the ellipsometric information is to plot the difference in p and s reflectivities vs the difference in ± 45° reflectivities (so-called A2-B2 curves). The trajectories of A2-B2 curves can be predicted and depend on such variables as the film index, thickness, absorption and gradients, but also on form birefringence, including microstructural parameters (i.e., void size and filling factor). Therefore, in-situ ellipsometric A2-B2 plots, coupled with a valid model prediction can be a convenient nondestructive tool to probe the microstructure of the films.

A2-B2 plots of films, deposited at constant rates (to minimize index gradients) and at O_2 pressures of 1.5-2×10^{-4} Torr (to minimize absorption) exhibited form birefringence effects. This was most pronounced for pure TiO_2 and TiO_2-rich films (up to 40% SiO_2) (Fig. 4). For TiO_2 concentrations below 60%, the trajectories changed to pure SiO_2 film trajectories. Apparently, the grain size and shape changes at approximately 50% concentration. These results were also confirmed by TEM analysis.

Water in the films can be completely removed by annealing. The annealing temperature for complete removal of water increases with the initial water content of the films. For example, films formed at low temperatures sorb more water and require higher annealing temperatures than films formed at high temperatures.

Annealing also improves the short and long range order in the crystalline structure of the film, as indicated by the increase in the intensity and reduction in the bandwidth of the phonon absorption bands (Fig. 5). Figure 5 also shows that the bending mode phonon changes from SiO-like to SiO_2-like after 500°C annealing.

2.1.3   Crystallization and Interdiffusion

High temperature annealing, that might be required to anneal SiO_2-TiO_2 films, can lead to crystallization of TiO_2. This is undesirable as it will generate bulk and surface scatter by segragation of TiO_2 (the high index material) in the low index matrix and by roughening the surface morphology due to uneven shrinkage in the film. It was observed that SiO_2 in the mixed films plays a beneficial role in regard to the above mentioned problems. The presence of SiO_2 reduces the rate of crystallization and the
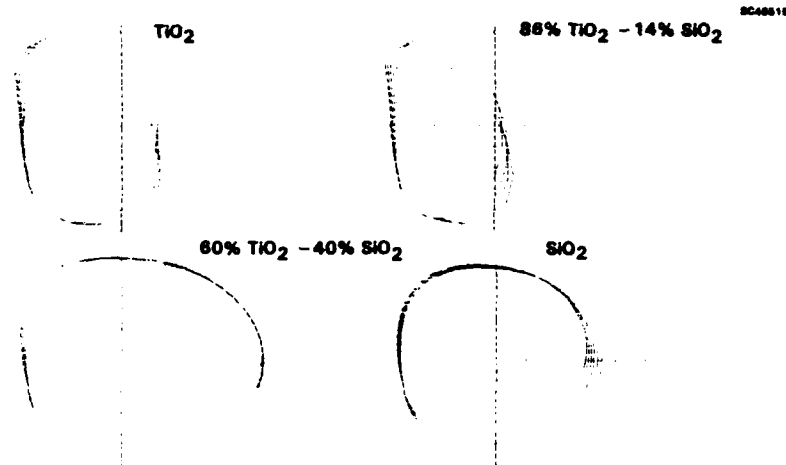
Fig. 4　In situ A2-B2 ellipsometric plots of TiO_2-SiO_2 films with different compositions.
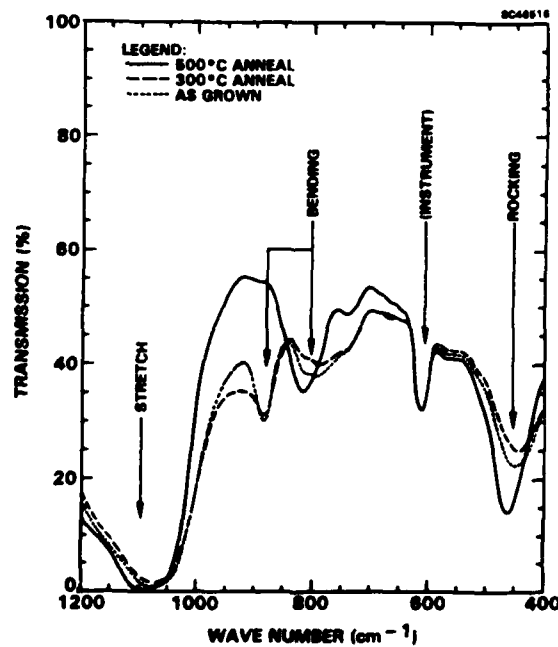
Fig. 5　Infrared transmission spectrum of a SiO_x film after consecutive annealing steps in air.

size of crystallites. It also preserves the inital smooth surface morphology, even in the case of extensive TiO_2 crystallization, probably due to the viscous nature of SiO_2 at high temperatures.

TiO_2 in mixed composition films crystallizes in anatase phase, at temperatures of ~ 600°C. The temperature to achieve a given degree of crystallization, as indicated by the grain size, increases with SiO_2 content.

The crystallization observed in analog mixed films occurs by de-mixing or segregation of TiO_2 out of the mixture, and coarsening of TiO_2 precipitates. Given the immiscibility in this binary system the non-equilibrium mixture proceeds toward equilibrium under annealing. Crystallization of TiO_2 occurs at temperatures of 600°C in intermediate composition films. However, segregation of TiO_2 could be occurring at lower temperatures with the formation of amorphous micrograins. This cannot be detected by XRD analysis because of noncrystalline nature of these regions, however high resolution TEM might resolve the microstructure of these regions.

Rutherford backscattering indicated that no interdiffusion occurred (Fig. 6) in digital structures. Digital films were observed to be very stable with respect to morphological degradation or interdiffusion even though sublayers of pure TiO_2 layers crystallized at temperatures as low as 400°C. These crystalline grains extend between the SiO_2 boundaries of TiO_2 layers, as indicated by x-ray diffraction studies (Fig. 7). In this figure there is one to one correspondence between grain size and TiO_2 layer thickness.

The crystallization studies have also yielded diffusion coefficients of TiO_2 in the composite matrix. These data are the first diffusivity data in mixed oxides to the best of the authors' knowledge.

These studies have generated information on deposition and post deposition conditions required to produce low stress, low water content, homogeneous, dense and morphologically smooth films.

Details of these results are presented in Appendix 2, titled "Crystallization and Diffusion in Composite TiO_2-SiO_2 Thin Films."

2.2   IR Systems

The materials used in this part of the study are all durable (for IR materials), environmentally stable and have broad wavelength ranges for transmission.

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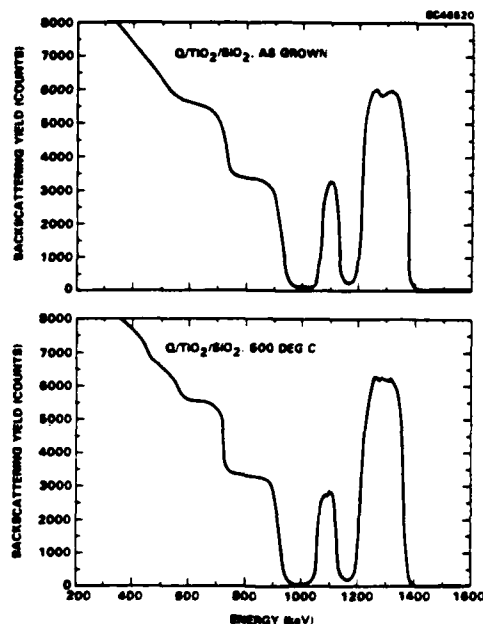
Fig. 6 Rutherford backscattering analysis of TiO_2/SiO_2 discrete layers (a) as grown, (b) after 500°C annealing, 8 hrs.

The stress in both $ZnSe-SrF_2$ and $Si-YF_3$ systems exhibits nonlinear dependence on composition. The behaviour in $Si-YF_3$ system is reminiscent of the behaviour that was observed in $Ge-MgF_2$, $Ge-CeF_3$ and $Ge-LaF_3$ systems.[6] It is attributed to the lowering of the intergrain surface energies in the intermediate composition films as the number of grains with unlike materials increases with composition.

In the $ZnSe-SrF_2$ system, we also observed optical scatter to vary nonlinearly with composition. Both intrinsic stress and optical scatter were observed to vary abruptly at 70% mole fraction SrF_2. This composition is not the boundary between ZnSe-like and SrF_2-like films but rather between different crystal orientations of SrF_2-like films. Here, SrF_2-like means that the SrF_2 crystallinity is dominant in the composite film.

The refractive index was measured as a function of composition in this system (Fig. 8). The behaviour is essentially linear. Small deviations are within the error in determining film composition and therefore we made no attempt to fit the data to any of the dielectric mixture models (e.g., Maxwell-Bruggeman, Lorenz-Lorentz).

Fig. 7

TiO$_2$ anatase grain size as indicated by the width of x-ray diffraction line vs TiO$_2$ layer thickness.
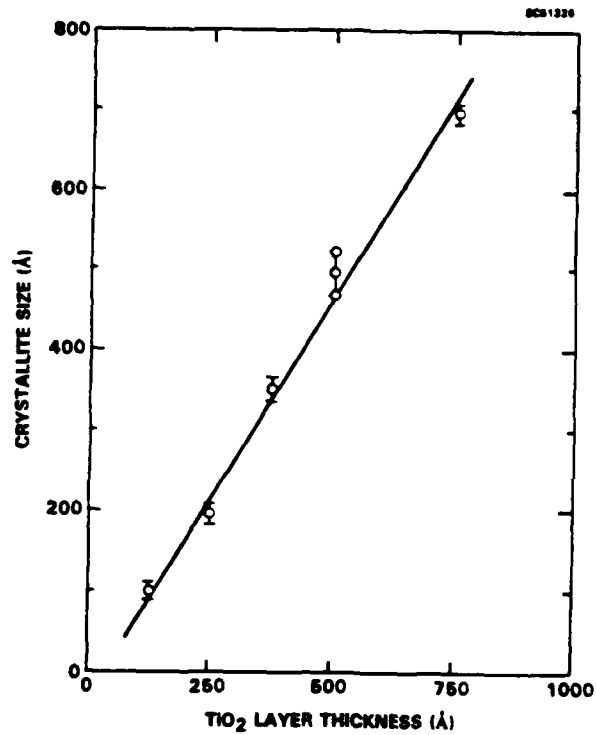
Fig. 8

Refractive index at 632.8 nm vs composition in the ZnSe-SrF$_2$ system.
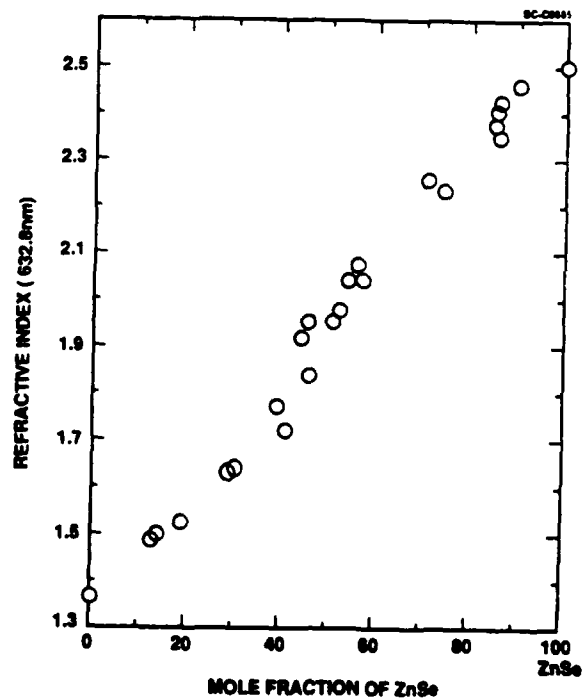
Details of these results are presented in Appendix 3, titled "Stress, Scatter and Structure Dependence on Composition in Thin Films of Si-YF$_3$ and ZrSe-SrF$_2$."

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3.0 CONCLUSIONS

These studies have indicated that composition strongly affects the properties of composite dielectric thin films. This effect is not only due to the "averaging" of the properties of the pure constituents in the mixture but also because of unique film microstructures engendered by the composite chemical environment during thin film growth. As a general conclusion, composite dielectric systems have physical properties that cannot always be predicted on the basis of the properties of the pure constituents that form the mixture. Many of the microstructure dependent properties, therefore, differ from the volume fraction weighted or linear averages of the pure material properties.

These results indicate that mixed composition systems behave in unique ways and that each system needs to be studied in detail for optimal overall film properties. Presently a general theoretical mechanism to predict the film microstructure and film properties is not available, save for general trends for the dependence of properties on deposition conditions.

In these studies the process conditions and compositions that produce films with low stress, smooth morphology, dense microstructure, and low or no water content have been established in the three material systems studied.

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Acknowledgment

5.0 APPENDICES

APPENDIX 1
SORBED WATER AND INTRINSIC STRESS IN COMPOSITE TiO$_2$-SiO$_2$ FILMS

Sorbed water and intrinsic stress in composite TiO$_2$-SiO$_2$ films

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Water sorption and stress properties of mixed composition TiO$_2$-SiO$_2$ thin films, formed by reactive evaporative codeposition, were studied. These properties were observed to depend on the composition, and also on the reactive gas pressure and annealing conditions. Process conditions to produce water-free films were established. Detailed stress studies in vacuum and in ambient indicated that intrisic stress also depends on ambient conditions, with irreversible changes occurring during the initial exposure of the films to ambient. This induced opposite types of stress on TiO$_2$- and SiO$_2$-rich films. These observations can be explained in terms of the structural and compositional properties of the films.

I. INTRODUCTION

Many novel optical coatings require synthesized materials, often obtained by mixing two or more constituents, to meet the requirements for optical (e.g., refractive index[1,2]) and mechanical (e.g., stress[3]) properties. Gradient-index optical devices are one such group of coatings that require continuous variations in index, hence, continuous variations in composition in the film growth direction. TiO$_2$ and SiO$_2$ form a useful binary material system in the visible and near-infrared wavelength range which has been used in many graded-index coatings, including rugate filters.[4] A rugate filter is a special reflective spectral filtering device that has a sinusoidal variation in index, hence composition, in the film growth direction.

In general, composition as well as deposition and post-deposition processing conditions strongly affect film microstructure, and therefore many of its macroscopic properties. Film properties do not always vary linearly with atomic composition and cannot be predicted by those of the pure constituents,[5] because the mixed films often have their own unique microstructure. Even small amounts of a compound in the mixture can cause significant changes in the microstructure.[6] The effect of ambient (e.g., water sorption) on the film properties also depends on the film microstructure and composition, that is, porosity and stoichiometry of the grain surfaces.

Often, the process conditions, microstructure, and ambient effects are interrelated. As an example, high oxygen pressures, required during deposition to minimize optical absorption, cause films to have a porous microstructure. The porous structure promotes moisture adsorption in the ambient, which in turn affects optical and mechanical properties. High-temperature annealing is used to densify the films. However, this process needs to be carefully controlled since it may also cause degradation of optical performance of the coating due to partial crystallization of amorphous materials, interdiffusion between the layers, structure-related alteration of index, or thermal stress-induced mechanical failure. This example illustrates the need for global optimization of the film properties and deposition conditions.

Evaporated dielectric films have porous microstructure, owing to low adatom mobility during deposition at low substrate temperatures.[7,8] In ambient, water is sorbed in the pores.[9-11] The presence of water in the pores increases the average film index, as the void index increases to that of water (1.33) and also causes absorption bands in the 2.5–3 and 6–7 μm IR regions (Fig. 1). It also causes significant changes in the intrinsic stress, which might result in mechanical failure due to excessive compressive or tensile stress.[12] Water may also facilitate cracking by breaking metal–oxygen bonds, especially at the stress zones.[13] Therefore, establishing deposition and annealing conditions that would produce low-stress, water-free, and dense films is of special interest.

In this work, we report on the structural and mechanical properties of the TiO$_2$-SiO$_2$ binary system. The dependence of these properties on composition (Ti to Si ratio), deposition and annealing conditions, as well as on ambient, is discussed. Film porosity was observed to increase with in-
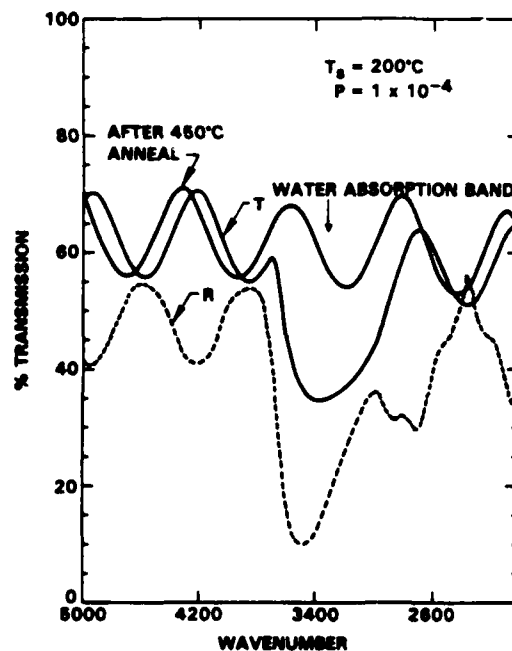

FIG. 1. IR transmission spectrum of a mixed composition (50% TiO$_2$) film as-grown (a) and after 400 °C anneal (b). Substrate temperature was 200 °C, deposition pressure 1 × 10^{-4} Torr O$_2$.

creasing gas pressure, but to decrease with increasing deposition and annealing temperatures. Optical properties (index and dispersion) exhibited a linear dependence on the Ti/Si ratio, whereas others (intrinsic stress) exhibited a markedly nonlinear dependence.

Detailed measurements of stress in vacuum, ambient, and at high temperatures indicated that water sorption in the ambient strongly affected intrinsic stress, inducing tensile and compressive stress in TiO_2- and SiO_2-like films, respectively. The stress became more compressive, or less tensile, with conditions producing denser structures such as SiO_2 content, high substrate temperature, and ion bombardment. High gas pressure had the opposite effect. Annealing also caused tensile, or less compresive, behavior due to shrinkage of the film. Both stress behavior and the sorbed water were related to the film microstructure, namely the presence of grains and the surface chemistry of these grains, in a unified model.

II. EXPERIMENT

Thin films of TiO_2 and SiO_2 and their mixtures were deposited on 100–300 °C substrates and under reactive gas pressures of 1–10×10^{-5} Torr O_2. O_2 was UHP grade with 0.1 ppm H_2O. The base pressure was 5×10^{-7} Torr in the deposition chamber at the beginning of the evaporation and typically lower at the end. Film thickness was in the 1–3μm range. TiO_2 was evaporated by an electron beam out of a stoichiometric source, whereas SiO_2 was obtained by thermal evaporation of SiO. A limited number of films were deposited under O_2 ion bombardment. The ion energies were in the 300–500 eV range and the ion flux was 50–100μA/cm^2.

A limited number of films with digital structure, consisting of very thin alternating SiO_2 and TiO_2 layers, were also deposited for purposes of comparison. Digital films consisted of ten 500-Å-thick pairs of layers. The relative thickness of pure TiO_2 and SiO_2 layers in each pair determined the effective composition. Annealing was performed in a tube furnace in air at temperatures of 200–700 °C and 100 °C intervals for times of 16 h.

Film composition was measured by energy dispersive x-ray analysis. Water content of the films was measured by IR transmission measurements of the samples after each annealing step (Fig. 1). The integrated area under the OH absorption peak at 3400 cm^{-1} was compared to peak height. Good correlation between these values indicated that peak width did not depend on the deposition conditions. Therefore, a relative measure of water was calculated using

$$(1/t)\ln(T_1/T_0),$$

where t is the film thickness, and T_1 and T_0 are optical transmission values at 3400 cm^{-1} of the film in ambient and of the same film if it had no water, respectively. The latter was obtained by reconstructing the transmission curve at the water absorption peak by using several adjacent interference extrema. IR transmission measurements were performed after sufficient time for the films to reach equilibrium with the ambient. Efforts to measure desorption kinetics by in situ IR transmission measurements are under way and will be reported elsewhere.

Films were etched in 3% by volume HF solutions with etch rates used as an indicator of the bond strain and porosity. Film stress was measured by the cantilevered beam technique using deflection of a laser beam to measure substrate curvature. The films exhibiting convex curvature on the film side were considered to be in compression and those with concave curvature in tension. Substrates were 0.015-cm-thick narrow strips of glass clamped to a fixture. The fixture had polished surfaces, which were used as a reference mirror, to measure the relative deflection of the cantilevered substrate. Thus, stress history of any sample could be studied by measurements in the deposition chamber, in the annealing furnace, in vacuum and ambient, by moving the fixture holding the sample into these environments. The rigidity of this fixture was tested using uncoated substrates during heating, cooling, and exposure to various ambients and was found to be such that only very small errors (20 kg/cm^2) were introduced. Measurements taken during heating and cooling gave stress values due to the difference in thermal expansion coefficients between the films and the substrate.

III. RESULTS

A. Sorbed water

The sorbed water in the films decreases with increasing deposition temperature (100–300 °C range) and increases with increasing gas pressure. This variation, however, is small compared to large reductions in the water content that can be obtained by annealing the films in the 200–700 °C range (Fig. 2).

Figure 2 shows the monotonic decrease in the water content with annealing temperature for films deposited at two extreme conditions, low pressure–high temperature (5×10^{-5} Torr, 250 °C) and high pressure–low temperature (1×10^{-4} Torr, 150 °C). Films grown at intermediate conditions exhibited a similar temperature dependence with the data falling between that of the above extreme conditions.
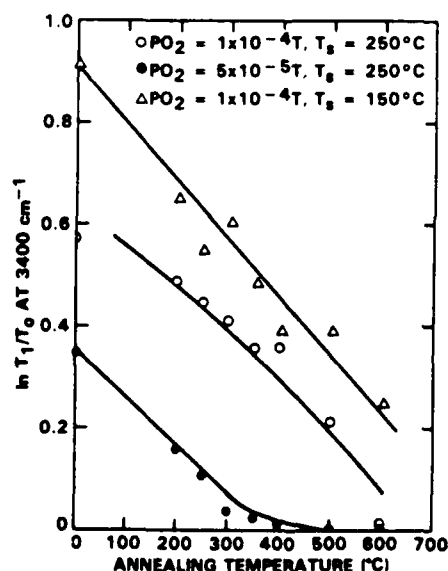

FIG. 2. Variation of water in the films with annealing temperature and deposition conditions.

The difference in the water content due to different temperature–pressure conditions, although small, is significant since it dictates the annealing temperature required to reduce the sorbed water to very low levels. The films deposited at low temperature and high pressures need to be annealed at 700 °C to achieve the same densification as the high-temperature–low-pressure films at 400 °C. Annealing at temperatures higher than 600 °C degrades the mechanical and optical properties of the coatings, as this process causes segregation in the TiO_2-SiO_2 system and crystallization of TiO_2,[14,15] stress-induced cracking and rough morphology in the mixed films. This can cause light scattering and loss of mechanical integrity of the film. Therefore, if water-free films and low annealing temperatures are desired, low gas pressures and high substrate temperatures must be used during deposition. The water sorption rate into the films slowed as the films became denser at high annealing temperatures, possibly indicating closing of the pores.

To clarify the role of the deposition pressure on the film porosity, water content of the films was studied as a function of the deposition parameters. These are listed in Table I.

As shown by the data in Table I, water content increased with the total pressure and the source-substrate distance, but was not affected by the partial pressure of oxygen or deposition rate. These data strongly suggest gas phase scattering and the consequent loss of thermal energy of the evaporants as the likely mechanism for film porosity. However, SiO films deposited in nitrogen are also water free, which indicates that stoichiometry or chemical state of the surfaces also plays an important role in adsorption. Ion-assisted deposition also produced water-free films as has been observed with many oxide dielectric materials.[16,17]

SiO_2 films exhibited a larger (by a factor of 2–3) water absorption peak than TiO_2 films deposited under the same conditions. This difference, which is probably related to the chemical nature of Si and Ti, persisted in the mixed films as the amount of sorbed water increased with the Si/Ti ratio (Fig. 3). An implication of these results is preferential sorption of water in the SiO_2-rich layers of a graded-index coating. This may distort the optical index profile as the increase due to sorbed water will be higher in SiO_2-rich layers than in TiO_2-rich layers.

Etch rate increased with deposition pressure, but decreased with deposition temperature (Fig. 4). These results also confirm that denser film microstructure is obtained at low deposition pressures and at high temperatures. Anneal-
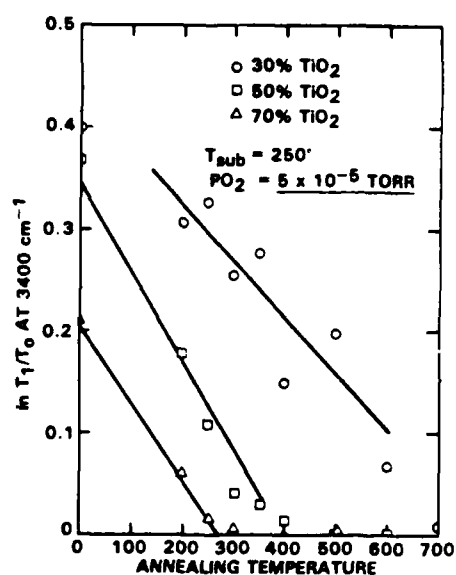

FIG. 3. Variation of water in the films with annealing temperature and composition. Note that water increases with SiO_2 content of the films.

ing decreased the etch rate, especially in porous films deposited at low temperature and high pressure. The incremental reduction in etch rate with annealing was high at low deposition temperatures and was roughly a factor of 5 for annealing at 500 °C.

B. Intrinsic stress

Film stress exhibited large and irreversible changes in the initial transition from vacuum to ambient air, probably due to chemisorption of water in the film pores. Additional changes occurred during annealing. These changes were often larger than the intrinsic stress of the sample in vacuum and the stress due to the difference in thermal expansion

TABLE I. Sorbed water for different pressure conditions.

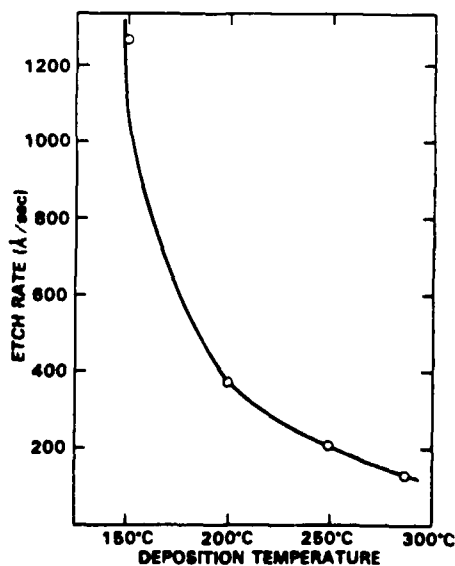| Pressure ($\times 10^{-5}$ Torr)	Source–substrate distance (cm)	Deposition rate (Å/s)	Relative water content
$10(O_2)$	20	4.0	1.0
$10(O_2)$	9	4.0	0.57
$5(O_2)$	20	4.0	0.62
$5(O_2)5(Ar)$	20	4.0	1.0
$10(O_2)$	20	8.5	0.9
$10(N_2)$	20	4.0	≈ 0
$10(400\text{-eV } O_2 \text{ ions})$		4.0	0

FIG. 4. Etching rate vs deposition temperature. Deposition pressure was 1×10^{-4} Torr O_2. Etchant was 3 vol % HF in H_2O.
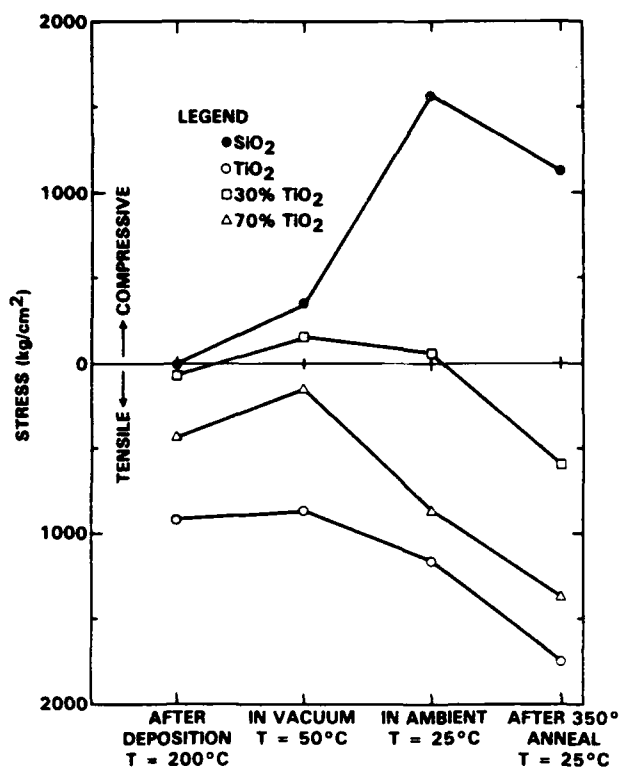
21

FIG. 5. Intrinsic stress in the mixed composition and pure TiO₂ and SiO₂ films in vacuum and air and after annealing. Deposition temperature was 200 °C.

TABLE III. Effect of deposition conditions and annealing on intrinsic stress.

Conditions	Type of stress
TiO₂-rich	Tensile
Temperature	Compressive
Pressure	Tensile
Annealing	Tensile
Ion bombardment	Compressive

in tensile stress during air exposure and annealing in TiO₂-rich films was often responsible for stress-induced cracking during annealing of thick (> 10 μm) films. Figure 5 also shows that pure TiO₂ has tensile stress in vacuum and mixed composition films have tensile stress increasing with their TiO₂ content.

Following air exposure and annealing, any further ambient effects on stress were observed to be reversible. In general, a vacuum environment and heating induced a tensile component of stress. Venting to air restored the stress value before the vacuum treatment. Thermal stress was measured in the 25–225 °C range. Thermal expansion coefficients of the pure and mixed films were calculated (Table II) using bulk modulus values for TiO₂ and literature values for SiO₂.

The dependence of stress on composition and deposition parameters is summarized in Table III. Here, the stress sign is used to indicate a trend rather than an absolute value.

Dependence of stress on composition is shown in Fig. 6 for codeposited and digital films. Both types of films exhibit a trend toward more tensile stress as TiO₂ content increases; however, this trend is more pronounced in digital films and

coefficients between the substrate and the film. Therefore, the stress values and their dependence on composition and deposition conditions are reported in vacuum at deposition temperature and in ambient air separately. The latter is of practical importance since the stress in atmospheric environment is what needs to be taken into account for mechanical stability of the coating, whereas the former represents the true intrinsic stress of the film. However, both stress values depend on the film microstructure as will be discussed in the next section.

The magnitude and sign (compressive or tensile) of stress induced by this ambient effect strongly depend on composition and deposition conditions, especially pressure. Upon exposure to ambient, TiO₂-rich films had tensile stress, whereas SiO₂-rich films exhibited compressive stress, indicating different underlying mechanisms or structural effects (Fig. 5). Annealing caused less compressive or more tensile stresses to develop for all types of films. This increase

TABLE II. Thermal expansion coefficients of SiO₂, TiO₂, and SiO₂-TiO₂ mixed films.

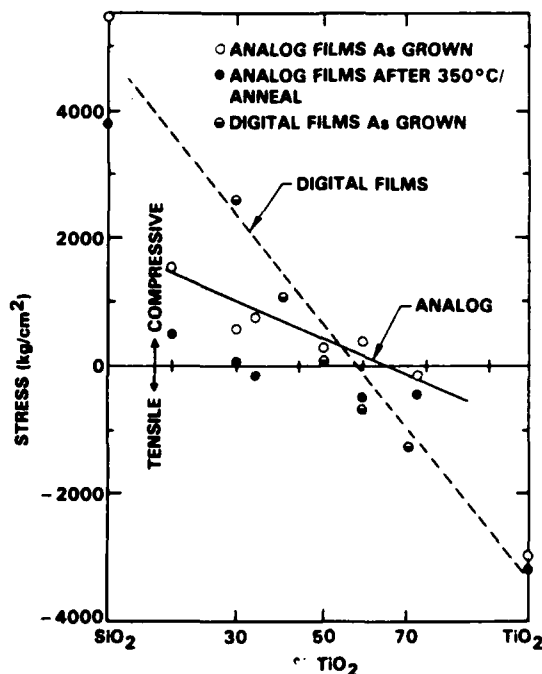| Material	Young's modulus (× 10⁶ ps)	Coefficient of thermal expansion (× 10⁻⁶/C)
SiO₂	3	2
TiO₂	13	7.5 ± 0.5
SiO₂-TiO₂(50%)	0.5(3) + 0.5(13)	5.4 ± 0.5

FIG. 6. Intrinsic stress vs film composition in codeposited and digital films. Deposition temperature was 250 °C and deposition pressure was 1 × 10⁻⁴ Torr.
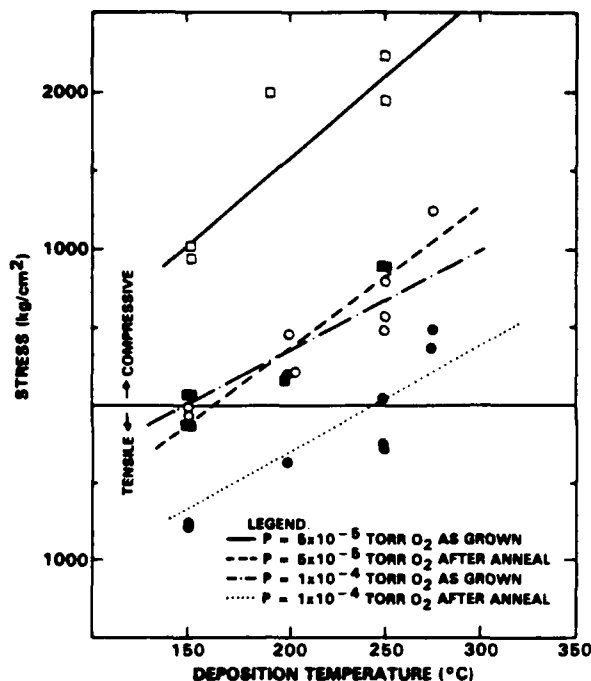
FIG. 7. Intrinsic stress vs deposition temperature at two different deposition pressures. 1×10^{-4} and 5×10^{-5} Torr. Film composition is 30 mol % in TiO_2.

which parallels the linear interpolation of the stress between TiO_2 and SiO_2. This behavior is similar to that observed for digital films of other material systems (e.g., ZnS-Ge, MgF$_2$-Ge).[5] Codeposited films generally exhibit lower stress and weaker dependence on composition than digital films. This nonlinear behavior has also been observed in several other binary dielectric systems.[5] Apparently alloying, even with
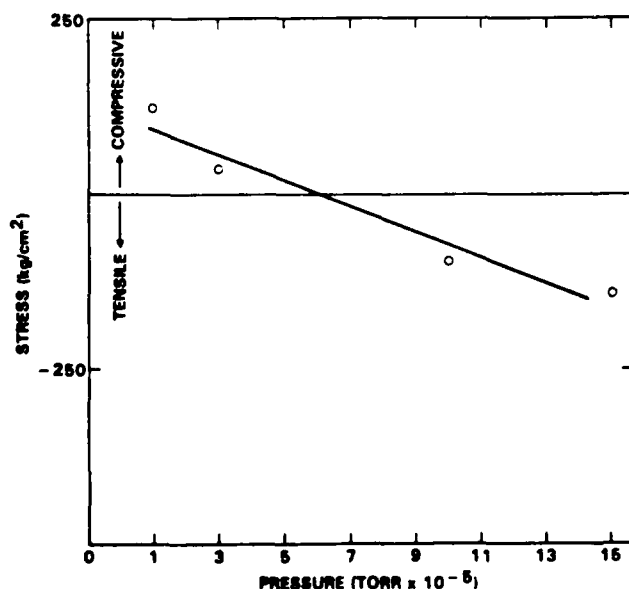

FIG. 8. Dependence of intrinsic stress. as measured in vacuum, on deposition pressure. Film composition was 50 mol % TiO_2 and deposition temperature was 200 °C.

small amounts of the solute, alter the microstructure so that stress behavior of mixed composition film is unlike that of the constituents (Ti and Si oxides).

The refractive index varied linearly with composition in mixed films. No deviation from a straight line interpolation was observed in the index-composition data, within error limits, even though effective medium theories predict such a deviation.[18]

Increasingly compressive behavior of stress at high temperatures (Fig. 7) and low pressures (Fig. 8) is related to the greater density of the film grown under these conditions. However, thermal strain due to expansion/contraction differential between the BK-7 substrate and the film also accounts for roughly half of the temperature dependence (Fig. 7).

O_2 ion bombardment during deposition makes the films less tensile (or more compressive) and also less sensitive to ambient and annealing, probably because of the dense and nonporous nature of the films grown with this technique. TiO_2 film stress, which was 2300 kg/cm^2 when deposited without ion assistance, decreased to 700 kg/cm^2 when the films were deposited with 100 μA/cm^2 O_2 ion current.

IV. DISCUSSION

A. Water sorption

The results on intrinsic stress and sorbed water can be explained in terms of film microstructure, especially porosity. Porosity arises due to limited adatom mobility, which, for a given species, depends both on the energy of the vapor species incident on the growth surface and on the substrate temperature. Experiments indicate that high temperatures and energetic vapor species (e.g., ions) promote dense structures, whereas high background gas pressures, by causing loss of energy of evaporant species via gas phase scattering, cause lower packing densities.

Our IR absorption measurement do not give an absolute quantitative measure of water because of lack of calibration. However, the amount of water can be estimated by the wavelength shift of the reflectance band of some optical coatings. The largest shift in the rugate filters grown with these materials was 3%–4% upon exposure to ambient. Assuming that the observed shift is given by an increase in the refractive index due to filling of the pores with water (refractive index = 1.33), the volume of water is estimated to be 2.5% of the film volume. Shintani, Sugaki, and Nakashima have made quantitative measurements[19] of the amount of water released upon heating of plasma CVD-grown SiO_2 films. The relative volume of water is also found to be 1%–2% of the film volume. Packing densities estimated from refractive index values, however, indicate a much larger void volume for TiO_2. The refractive index for fully oxidized SiO_2 films was 1.45 + 0.01, which suggests close to unity packing density. Higher water content of SiO_2-rich films in spite of lower pore volume in these films suggests that the relation of sorbed water to pore volume or pore surface area may depend on the material or surface chemistry of the pores.

Annealing reduces the sorbed water and the rate of water adsorption, as has also been observed in SiO_2 films deposited by CVD[20] and plasma CVD.[21] Two possible mecha-

nisms are sintering (i.e., closing of the pores) and a decrease in the concentration of adsorption sites at the grain surfaces. Surface profilometric measurements did not indicate any shrinkage of the SiO_2 films to an accuracy of 1%. Since the pore volume occupied by water is about 2% of the film thickness, these measurements could not rule out sintering. TiO_2, on the other hand, undergoes significant volume reduction upon annealing,[22] and therefore mixed composition films are expected to undergo shrinkage during heat treatment. Two possible adsorption sites for the OH^- radical are unoxidized metal atoms or strained and dangling bonds. The concentrations of both are reduced by air annealing, as indicated by lower UV absorption and lower etch rates, respectively. Therefore, both of the above mechanisms, sintering and modification of grain surface chemistry, may be responsible for reduced water in the annealed films.

B. Intrinsic stress

The effect of moisture adsorption on stress depends on the material, being compressive for SiO_2 and tensile for TiO_2. A widely accepted model[10] based on OH^- dipoles protruding normal to the grain boundary surfaces and repelling dipoles on the opposite grain surface predicts compressive stress. Increasing compressive stress observed in SiO_2 and in SiO_2-rich films deposited at low pressures supports this model.

TiO_2- and TiO_2-rich films, on the other hand, have lower packing density but also less water than SiO_2-like films. Therefore, adsorbed OH^- dipoles probably have more freedom to align so as to reduce repulsive electrostatic energy. In fact, they probably assume a lower-energy configuration that would enhance attractive electrostatic forces between them or that could even promote hydrogen bonding between sites on opposing grain surfaces. The above would enhance attractive forces between the grains, and hence increase tensile stress.

In both of the above cases, the thin-film substrate system minimizes its total energy, which consists of strain, surface, and dipole interaction energy contributions. This constraint determines the extent of surface coverage by water, the position and bonding of adsorbed OH^- groups, and the resulting strain in the film. Thus, the sign and magnitude of stress caused by water adsorption depend on features of structural defects such as pore size and surface area of columnar grains as well as the chemical state of these surfaces. The driving force is the lowering of the surface energy. Increase in tensile stress and reduction in compressive stress in the annealed films may be accounted for by reduction in pore volume, and the resulting shrinkage in the film.

V. CONCLUSION

Water sorption and intrinsic stress properties of codeposited TiO_2-SiO_2 films have been studied. The amount of sorbed water increased with SiO_2/TiO_2 ratio and with deposition conditions such as high background gas pressure that promoted a less ordered and lower packing density structure. Annealing reduced the water content of the films. Lower annealing temperatures (400 °C) are required to elimi-

nate water from the low porosity films (deposited at 300 °C and at 5×10^{-5} Torr O_2 pressure) than those having more water in the as-grown state.

Intrinsic stress was measured in vacuum after deposition, after exposure to ambient, and after annealing. In vacuum, all films had tensile stress, which increased from nearly zero to moderate (1000 kg/cm^2) values as the composition varied from pure SiO_2 to pure TiO_2. Water sorption in air increased this tensile stress to larger values. SiO_2 films, on the other hand, became more compressive. Annealing generated a tensile component of stress.

These studies indicate that both microstructure and chemical state of the surface are important in determining the type and magnitude of stress. Microstructures with high porosity, as would be generated at low temperatures, high pressures, and in high TiO_2 content films, have high tensile stress. Denser structures, such as would be generated by ion-assisted deposition, or at high temperatures, have less tensile or more compressive stress. Water sorptivity and its dependence on SiO_2 content also plays a role and generally induces compressive stress. These quantitative results will be helpful in establishing deposition parameters to produce films with low stress and low porosity.

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APPENDIX 2
CRYSTALLIZATION AND DIFFUSION IN COMPOSITE TiO_2-SiO_2 THIN FILMS

CRYSTALLIZATION AND DIFFUSION IN COMPOSITE TiO_2 - SiO_2 THIN FILMS

H. Sankur and W. Gunning

The crystallization behaviour of evaporated TiO_2-SiO_2 mixed composition films and its dependence on composition, temperature, time, and type of mixing (codeposited or alternating layers) were studied. All codeposited films annealed between 600-900°C with 15-90% molar TiO_2 exhibited crystallization in the anatase phase. Crystallite size increased with Ti content of the film and with temperature. TiO_2 in alternating layered films, which had layer thicknesses in the 65-1000Å range, crystallized in the anatase phase in the 400-600°C range, with thin layered films requiring higher temperatures for crystallization. For temperatures of 900-1100°C, codeposited films transformed into rutile whereas alternating layered films remained as anatase. Diffusivity of Ti in the mixed composition film was calculated to be 3×10^{-14} and 3×10^{-13} cm^2/sec from the study of precipitation kinetics at 950° and 1050°C, respectively. Morphology of intermediate composition analog films (25-65% atomic TiO_2) remained virtually unaltered from its as-deposited state after annealing and crystallization.

INTRODUCTION

TiO_2 and SiO_2 are commonly used materials in optical thin film filters in the visible and near infrared ranges. Thin films of these materials formed by vapor deposition are hard, chemically stable and have a large refractive index difference. The large range of intermediate index values that can be obtained by mixing these materials also makes them desirable in gradient index coatings (R1). Gradient index coatings can be

made by (a) codeposition of TiO_2 and SiO_2, where the rates of evaporation determine the film composition, hence the index, and (b) alternately depositing very thin (a small fraction of the design wavelength) layers of the individual materials, where the ratio of the layer thicknesses determines the composition (alternating layered).

TiO_2 has a high dielectric constant and therefore can also be used in microelectronic applications, often in contact with SiO_2 layers.

Optical coatings can be subjected to high temperatures during processing (e.g., annealing) or in use (laser or energetic particle irradiation). Thin films of pure TiO_2 crystallize in the anatase phase at temperatures of ~ 350°C and in the rutile phase at temperatures of 600°C and above.[2] Since TiO_2 and SiO_2 are immiscible[3,4] any crystallization in the analog mixed films implies segregation or exodiffusion of Ti. Segregation and crystallization can degrade optical properties since the resulting inhomogenous structure consisting of high refractive index (~ 2.4) crystalline TiO_2 embedded in the silica rich, low index matrix can cause considerable scatter. Shrinkage occurring as a result of transformation from the vapor deposited, amorphous state into crystalline anatase, and from anatase into rutile, could cause development of large strains or even loss of mechanical integrity of the films.

Addition of small amounts of a glass forming solute (e.g., SiO_2) into some oxides has been reported to prevent (R5, R6) crystallization of the host material. Admixture of SiO_2 into sputter deposited TiO_2 films was also observed to retard crystallization.[7] Therefore, we are interested in establishing compositions and the respective maximum temperatures and heating times that prevent formation of crystalline phases in this system.

Below a certain critical thickness (~ 500Å), crystallization in pure TiO_2 films is inhibited (R8). This has been attributed to the increasing role of surface energy as the area to volume ratio increases with decreasing film thickness. Since digital films consist of layers at or below this critical thickness, we also need to study TiO_2 crystallinity in these structures and establish layer thicknesses that might retard or suppress TiO_2 crystallinity for the commonly used processing temperatures.

Crystallization and phase segregation in codeposited and alternating layered TiO_2-SiO_2 films were studied by X-ray diffraction and TEM analysis. All annealed codeposited films with compositions within 15-90 molar% TiO_2 exhibited crystallinity in the anatase phase. The rutile phase formed in codeposited films starting at 900°C but was not observed in alternating layered structures under any of the high temperature treatments including a 72-hour anneal at 1100°C. Anatase crystallite size decreased and the tendency to form rutile increased as the TiO_2 content in the codeposited films increased. Codeposited films with intermediate compositions (25-65% molar TiO_2) and alternating layered films with layer thicknesses less than 125Å remained amorphous when annealing temperature did not exceed 600°C. These films retained the smooth morphologies under all annealing conditions. These studies defined the limits of heat treatment conditions that would not cause significant crystallization and diffusion and that would not alter the surface topography of evaporated mixed composition TiO_2-SiO_2 films.

EXPERIMENTAL

Thin films of mixed composition were prepared by reactive deposition of e-beam evaporated TiO_2 and thermally evaporated SiO. Deposition pressure was

1×10^{-4} Torr O_2. The substrates were quartz and Si and the substrate temperature was 200°C. The deposition rate for each constituent was in the 2-5Å/sec range and the film thickness was 1-1.5 microns.

Codeposited films composition was determined by X ray dispersive analysis of films deposited on vitreous carbon substrates.

Alternating layered films were formed by sequential deposition of thin layers of pure SiO_2 and TiO_2 pairs. To study the effect of thickness on crystallization, thicknesses of 65, 125, 250, 375, 500, 750 and 1000Å were used for the pure material layers in the alternating layered films. This range comprises thicknesses encountered in optical coatings, since 65Å is a typical layer thickness for digitally synthesized composite films for the visible range, whereas 1000Å layers could be used for near IR (0.9 micron wavelength) high reflectance designs. Total film thickess (1 micron) and the average composition remained constant in the digital films while the number of layers decreased from 160 to 10 for the above sequence of thickness values. Since the amount of TiO_2 was the same in all the digital films, any differences in crystallinity could be interpreted as being due to thickness effect.

The films were isochronally annealed in air in the range 400-1100°C at 100°C intervals for 16 hours. Phase transformation kinetics was studied by isothermal anneals for different times. Film crystallinity was studied by X-ray diffraction (XRD); both diffraction intensity and diffraction line broadening were analyzed. The instrumental line width in the XRD apparatus was determined to be 0.15 degrees by using a commercially available Si wafer with <111> orientation. Transmission electron microscopy was used to study the nucleation density and particle shape of the anatase crystallites. SEM and optical microscopy were used to study the film surface and cross sectional morphology.

RESULTS

Codeposited Films

X-ray diffraction studies indicate that all codeposited films with compositions in the 15-90 atomic% range crystallize in the anatase phase of TiO_2 after annealing. However, mixed composition films with 80% or less TiO_2 require higher annealing temperatures ($\sim 600°C$) to crystallize than pure TiO_2 films, which become partially crystalline at $\sim 350°C$ (R2). The lattice spacing of the anatase phase did not depend on the initial composition of the films, indicating that pure TiO_2 precipitates out of the mixture, a result that corroborates the immiscibility in this system.

The size of anatase crystallites increases with TiO_2 concentration and temperature during isochronal annealing (Fig. 1). Particle size is deduced from x-ray diffraction line broadening using the Scherrer formula (R9), where any contributions to broadening due to nonuniform stress are neglected. Figure 1 shows that the linear dimensions of the TiO_2 crystallites roughly scale with TiO_2 content. TEM analysis indicated that the nucleation density increases with SiO_2 content of the films, so that numerous small crystallites characterized intermediate TiO_2 concentration films, but fewer and larger crystallites were observed in pure TiO_2 films (Fig. 2). The role of diffusivity, TiO_2 concentration, and nucleation density on the particle size will be discussed below.

Film composition also affects the dominant orientation of TiO_2 crystallites, which was <100> for low TiO_2 concentrations (<65%) and <101> for high TiO_2 concentrations (>65%).

Transformation from anatase to rutile occurs at temperatures above 900°C. This transformation depends on the initial film composition, occurring more rapidly for films with low TiO_2 concentration (<65%) than for films with higher TiO_2 concentration (>65%). These properties are summarized in Table 1.

Table 1
Dependence of Crystallization Properties on Composition

Composition	Grain size	Preferred Orientation	Conversion to rutile
TiO_2 rich	large	101	sluggish
SiO_2 rich	small	100	rapid

The time dependence of grain growth is shown in Fig. 3, where the 100 anatase diffraction linewidth is plotted vs square root of time. The observed time dependence suggests diffusion limited grain growth. These data were used to calculate diffusivity and its activation energy as explained below.

Diffusion

An estimate of Ti diffusivity in the mixed composition film was obtained from the analysis of crystallite growth or precipitation kinetics. An analytical study of solute precipitation (R10) shows that the precipitate grain dimension (a) depends on the diffusivity (D), time (t), and initial solute concentration in the mixture (c_0) and in the precipitate (c_1) as

$$a = \sqrt{(2\ c_0/c_1 * D * t)}$$

Here we have the simplifying assumption that the Ti concentration in equilibrium with the precipitate is 0, due to immiscibility in this system. Figure 3 represents the time dependence of particle dimension (a). Using the slope of this plot, diffusivity values of 3×10^{-14} cm^2/sec and 3×10^{-13} cm^2 are obtained for 950°C and 1050°C respectively, in a 50 molar% TiO$_2$ film ($c_0 = 0.5$). The activation energy calculated from these two diffusivities is 1.67 eV.

RBS analysis indicates that evaporated SiO$_2$ and TiO$_2$ films do not interdiffuse after annealing at temperatures of 1000°C. However, segregation and therefore outdiffusion of TiO$_2$ and SiO$_2$ (or Ti and Si in the oxide matrix) occur, as is evident from the precipitation and growth of TiO$_2$ crystallites.

Alternating Layered Films

All alternating layered films with TiO$_2$ layer thicknesses in the 65Å-1000Å range crystallized in the anatase phase during annealing. Films with TiO$_2$ layer thicknesses greater than 375Å exhibited crystallinity at temperatures of 350-400°C, whereas thinner layers (<250Å) required higher temperatures. 65Å layer films exhibit diffraction only after annealing at 600°C. The grain size, as deduced from diffraction line broadening, was comparable to the layer thickness. This result suggests that the crystallites extend between the two SiO$_2$ layers bounding each TiO$_2$ layer. All digital films, except for the films with the thinnest and thickest layers, remained in the anatase phase and never transformed into rutile even for prolonged (72 hrs) annealing at the highest temperature (1100°C). The thinnest layer (65Å) film converted into rutile starting at 900°C, with a behaviour similar to that of a codeposited film with intermediate composition, as discussed above. Prolonged annealing resulted in crystallite sizes exceeding the initial layer thickness, suggesting that layer sequence may have been

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destroyed and TiO_2 from 65Å layers may have diffused to form large crystallites. The film with 1000Å layers exhibited very weak rutile diffraction lines after the long anneal.

Morphology

Film morphology after high temperature annealing showed very strong dependence on composition. Figure 4 shows surface and cross sectional topography of pure TiO_2 and mixed composition films after 1000°C annealing. Pure TiO_2 undergoes a volume reduction upon crystallization resulting in the formation of large voids between interconnected and faceted islands (Fig. 4a). The volume reduction can be estimated by the increase in the refractive index from 2.15 of the as-deposited amorphous films to 2.4-2.5 of the dense and partially crystalline films. Neglecting the effect of absorbed water on the index of the as-deposited films, a density increase of over 12% is calculated from the above index values. Using literature values for the density of the anatase and rutile phases, a further volume reduction of 11% is calculated for the anatase to rutile transformation. The rough morphology of these films causes considerable optical scatter. Surface roughness of the films decreases with increasing SiO_2 content, with 60-90 molar% TiO_2 films exhibiting granular morphology with 1000-2000Å size grains (Fig. 4b). Films with lower TiO_2 concentrations (15-50 molar %) retain the smooth morphologies of their as deposited state (Fig. 4c).

DISCUSSION

Initial film composition affects the anatase crystallite size in codeposited films under isochronal annealing as seen in Fig. 1. For a given annealing condition, films with low TiO_2 concentration develop crystalline particles that are too small to affect the

33

optical properties. For instance, crystallites smaller than 100Å (40% TiO_2) are only 1/25 of the wavelength of light of 5000Å.

Crystal dimensions increase roughly by a factor of 2 with a doubling of TiO_2 content. The corresponding increase in volume, or amount of TiO_2 in the precipitate, is therefore a factor of 8. If segregation for all compositions proceeded to completion, the fact that for a given increase in the TiO_2 concentration in the initial mixture the amount of TiO_2 in each crystallite increases by a much larger factor, suggests lower nucleation density for higher TiO_2 content films, from Ti mass conservation. This is observed under TEM analysis (Fig. 2).

The composition dependence of anatase-rutile transformation kinetics depends on the anatase particle size, which decreases with decreasing Ti content in codeposited films. If rutile growth implies dissolution of the anatase phase and diffusion of Ti, it is expected that small and less stable anatase crystallites will transform more readily than larger and thermodynamically more stable particles. Pressure (P) lowers the transformation temperature (T), such that $dT/dP = 0.02°C/bar$ (R11,R12) as the reaction becomes thermodynamically more favorable under high pressures, probably due to the volume reduction accompanying the transition. Thin film stress during high temperature anneal could not be measured. However, using the stress data obtained at low temperatures (350°C) in the first part of this study (R13), films with low TiO_2 content, which exhibit rapid conversion to rutile, may have higher compressive stress, which favors the anatase to rutile transformation. However, plastic flow of SiO_2[14] and fracturing of the films with high TiO_2 content should alleviate most of the stress in the films. This, and the observation that the results did not depend on the type of substrate (Si and quartz differ significantly in their thermal expansion behavior and therefore would have produced

significantly different thermal strain), suggests that stress does not play a major role in this phase transformation.

The plastic nature of SiO_2 at the high annealing temperatures probably also accounts for the observed smooth morphology of the films with greater than 40% SiO_2. Apparently SiO_2 accommodates the volume shrinkage of TiO_2 resulting in the preservation of the integrity of the film, in contrast to generation of large voids in pure TiO_2 films (Fig. 4). The island morphology of the annealed TiO_2 films (Fig. 4a) might also be explained by the relocation of the material in the TiO_2 grains driven by the energy of the surfaces at the grain boundaries and at air and substrate interfaces, since analogous morphologies have been observed for ZrO_2 and Y_2O_3-ZrO_2 alloy films.[15]

Conclusion

The study of the structural properties of mixed composition TiO_2-SiO_2 thin films indicates that both the composition and the method of mixture (i.e., layered or codeposited) strongly affect the crystallization of TiO_2. The minimum temperature for the formation of anatase increases with decreasing TiO_2 content in the codeposited films and with decreasing film thickness in layered films. Growth of crystal particles in codeposited mixtures, which was observed to be diffusion limited, also decreases with decreasing TiO_2 content. Diffusivity of Ti was obtained from particle growth kinetics.

Optically equivalent alternating layered and codeposited mixed films exhibit different TiO_2 crystallization characteristics. Data presented above will allow us to tailor film preparation and annealing conditions, to suppress or to enhance TiO_2 crystallinity in the mixed composition films.
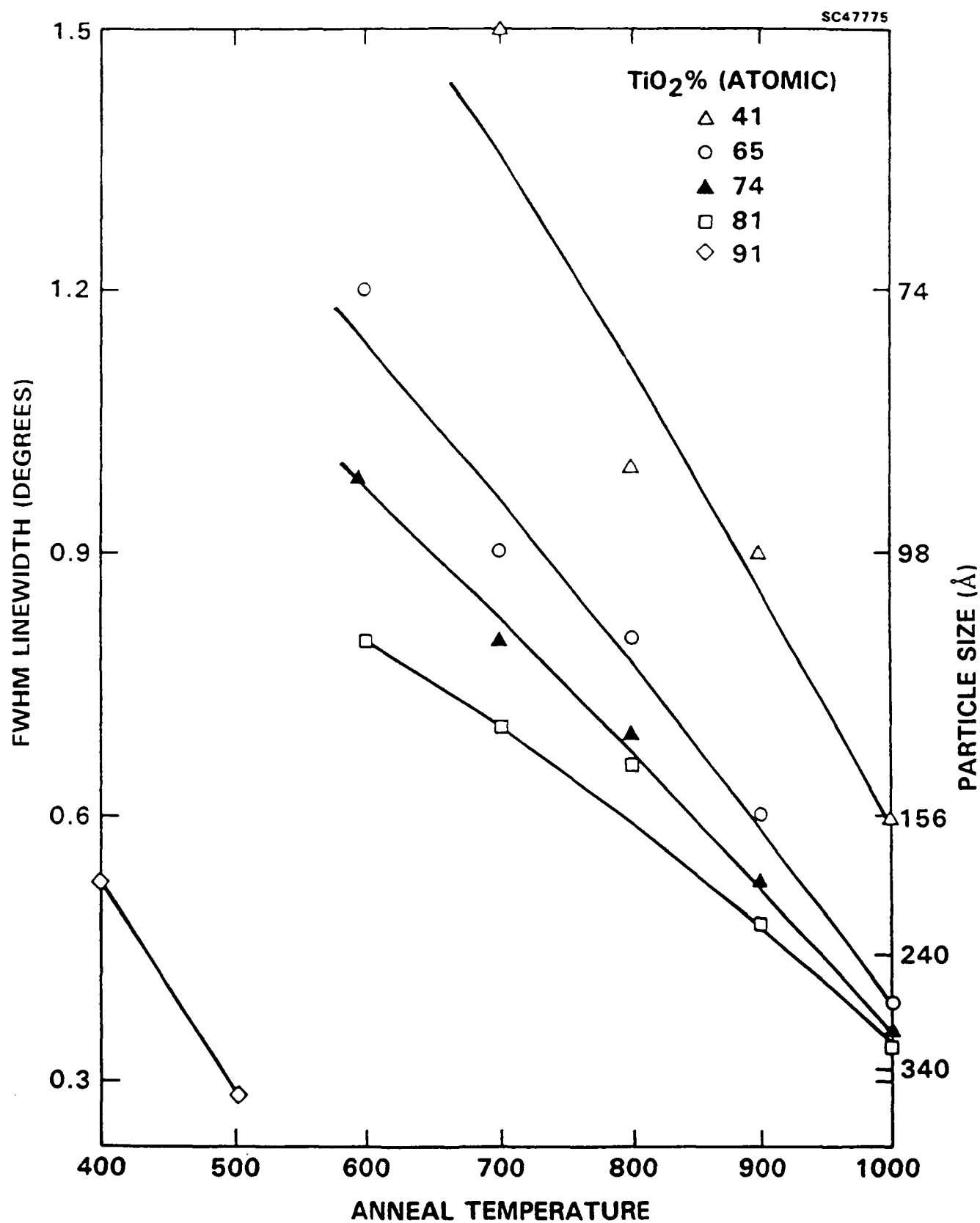
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Figure Captions

Fig. 1   Full width at half maximum diffraction line width in angles vs annealing
         temperature for codeposited films. The diffraction line is from 004 plane of
         anatase at 25.34 degrees and annealing time is 16 hours for all compositions
         and temperatures.

Fig. 2   TEM micrographs of annealed films showing the nucleation density and the size
         and shape of anatase crystallites. (a) TiO_2 annealed at 400°C; (b) 65% TiO_2-
         35% SiO_2 annealed at 700°C.

Fig. 3   Inverse of diffraction line width vs square root of annealing time.

Fig. 4   SEM micrographs showing surface and cross sectional topography of thin films
         after 1000°C, 16 hour anneal.   (a) pure TiO_2, (b) 80 molar% TiO_2, (c) 50
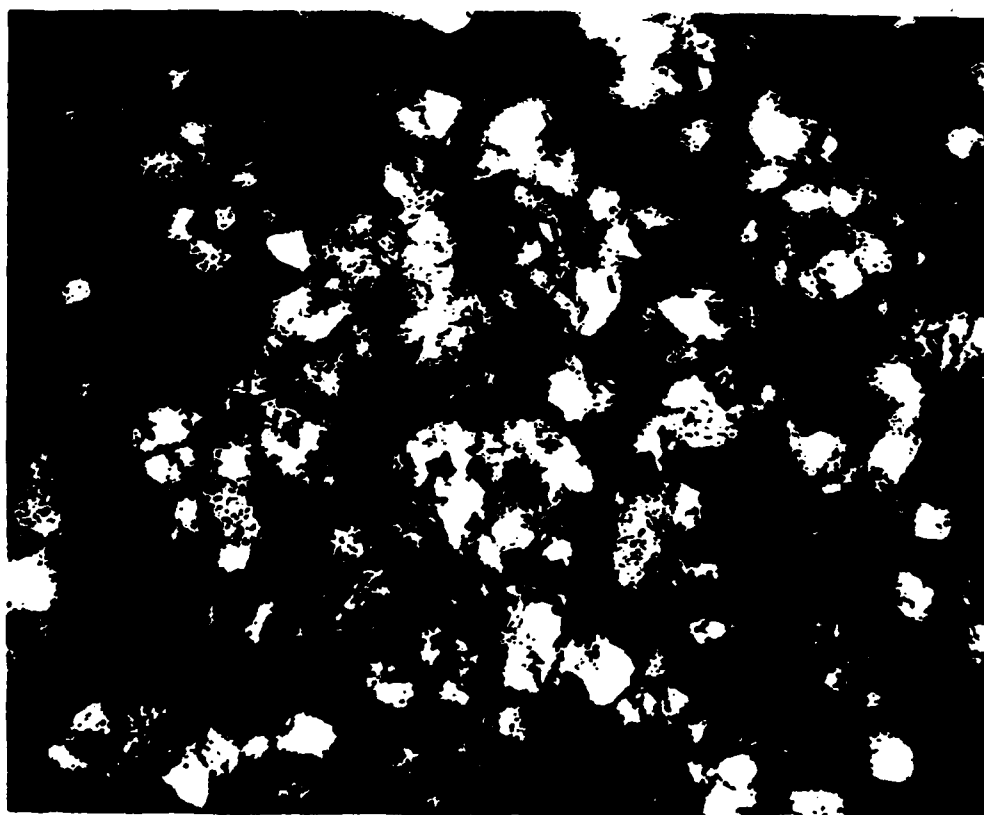   molar% TiO_2.

SC47775

FWHM LINEWIDTH (DEGREES)

PARTICLE SIZE (Å)

ANNEAL TEMPERATURE

TiO$_2$% (ATOMIC)
△ 41
○ 65
▲ 74
□ 81
◇ 91

39

FIGURE 1

1 μm

(b)

1 μm

(a)

40

FIGURE 2

SC-C0365

FIGURE 3

41

100% TiO$_2$

SURFACE

CROSS SECTION

80% TiO$_2$

SURFACE

CROSS SECTION

50% TiO$_2$

SURFACE

CROSS SECTION

42

FIGURE 4
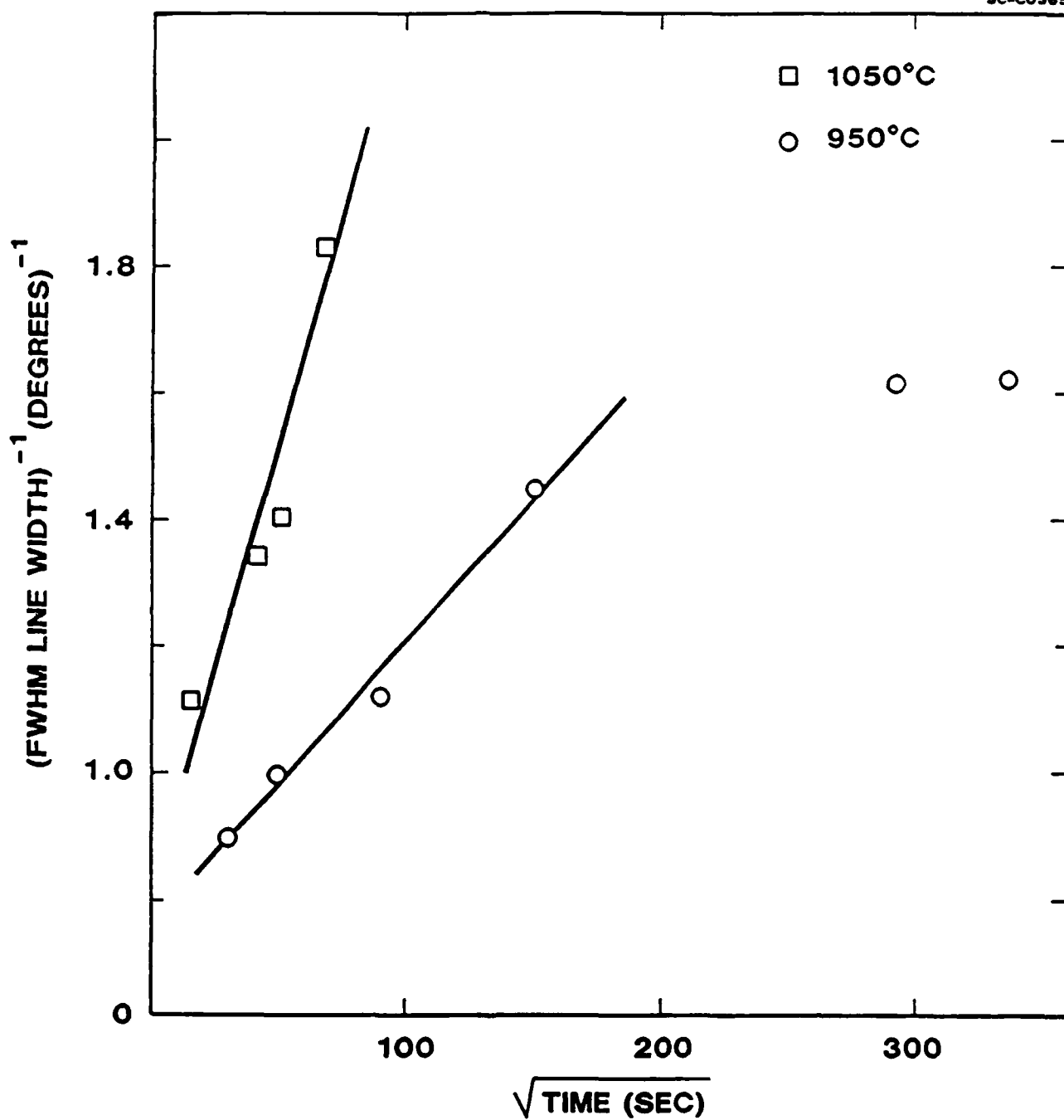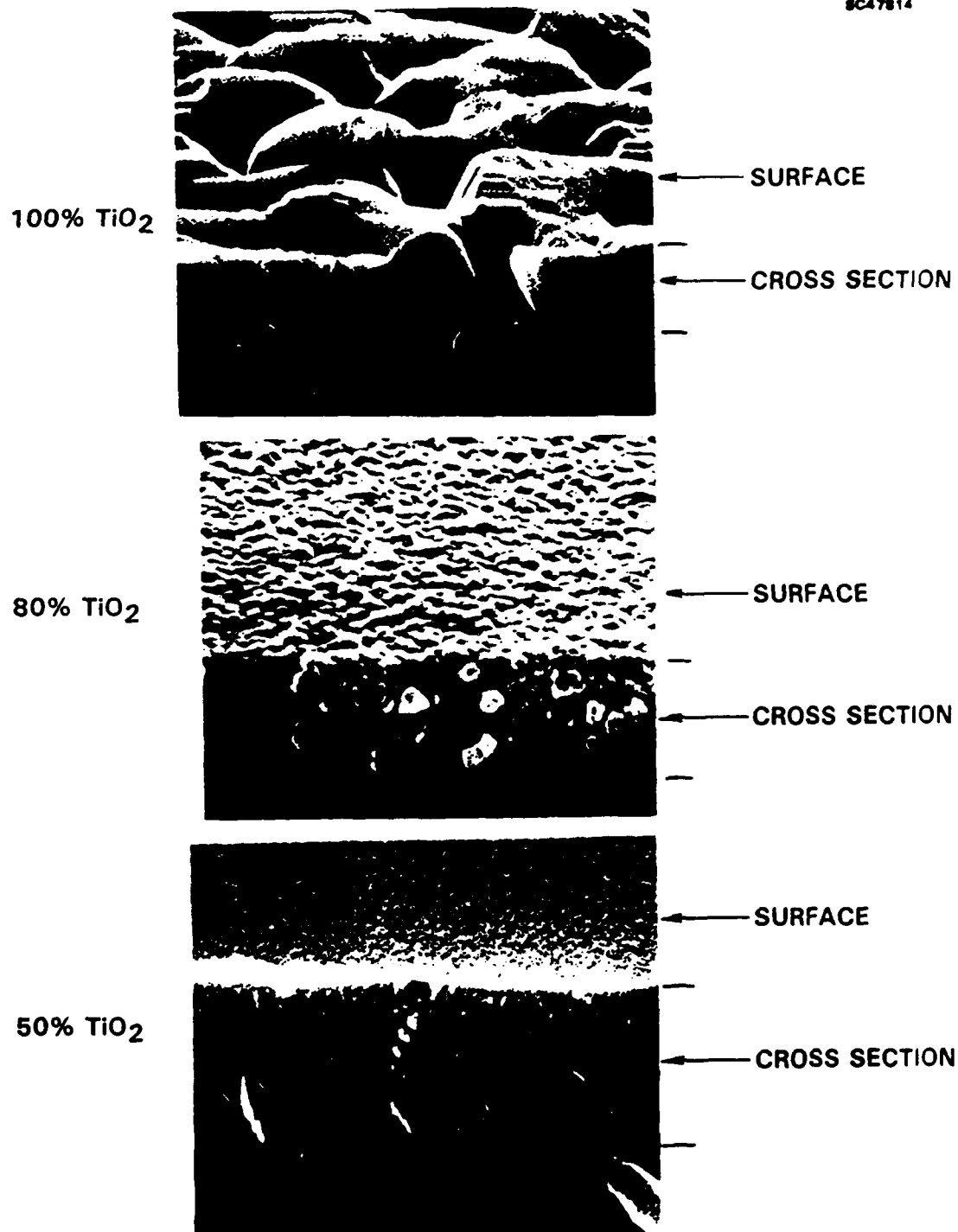
APPENDIX 3
STRESS, SCATTER AND STRUCTURE DEPENDENCE ON COMPOSITION IN THIN FILMS OF $Si-YF_3$ and $ZnSe-SrF_2$

STRESS, SCATTER AND STRUCTURE DEPENDENCE ON COMPOSITION IN THIN FILMS OF SI-YF$_3$ AND ZNSE-SRF$_2$

H. Sankur, J. DeNatale, W. Gunning

Abstract

Composition-dependent structural, optical and mechanical properties of codeposited thin films were studied in the Si-YF$_3$ and ZnSe-SrF$_2$ systems. Intrinsic stress varies nonlinearly in both systems. In the Si-YF$_3$ system, the stress becomes slightly compressive for intermediate compositions, even though it is highly tensile in the pure constituent thin films. In the ZnSe-SrF$_2$ system, optical scatter and intrinsic stress exhibit abrupt changes at ~ 60 vol% SrF$_2$, accompanied by a change in the dominant crystalline orientation. Possible structure-property relationships and composition ranges for practical applications of thick films are also discussed.

Introduction

Gradient index thin film technology requires materials exhibiting a large range of refractive index values and the ability to realize any index value in this range at a particular thickness in the thin film structure. Such materials can be obtained by alloying or mixing two or more of the commonly used optical materials and by carefully controlling the material composition as a function of thickness.[1]

The refractive index values of mixed composition films generally deviate only slightly from a linear dependence on composition[2] and can be modeled using a theory (e.g., Maxwell-Garnet) of dielectric mixtures.[3]

Some of the mechanical (e.g., stress) properties of the mixed composition films, however, cannot always be predicted on the basis of volume fractions and the values for the pure constituents, and deviate considerably from a linear dependence.[4,5] These properties are closely related to the film microstructure. For a given set of deposition conditions, the crystalline structure and the porosity of the evaporated thin films will depend on the inter-atomic and intergrain forces, the miscibility, and the mutual effect of the constituents on the adatom surface mobility during deposition. Crystallinity in immiscible systems is often suppressed for intermediate compositions and generally the degree of crystallinity does not vary linearly with composition. Since intrinsic stress strongly depends on the film microstructure as well as on intergrain forces, it is also often not a linear function of composition.

The nonlinear dependence of stress on composition suggests that each material system must be studied to determine the range of compositions and conditions that will produce low-stress or stress-free films. Stress properties can dictate the choice of material system for a particular optical coating to avoid stress-induced failure, especially for infra-red coatings where film thicknesses are large.

Microstructure affects moisture penetration into the film due to its porosity. Water in the film will cause absorption bands in the infrared, which can adversely impact coating performance. Optical scatter also depends on the film microstructure. Light scattering can occur due to rough surface morphology (surface scattering) or segregation and formation of regions of differing refractive index values in the bulk of the film (bulk

scattering). The grains can vary in size and orientation and can consist of crystalline regions, or regions of higher density in the void network of low temperature deposited dielectric films.

To assess the practical usefulness of thin film materials and to understand the nature of thin films, it is therefore of interest to study both the mechanical and optical properties of mixed composition thin films and to relate these properties to film structure. In this paper we report the crystallinity, morphology, refractive index, optical scatter, and the intrinsic stress properties of two binary systems: ZnSe-SrF_2 and Si-YF_3.

Each of the materials used in this study are chemically stable and are useful coating materials in the infrared, covering the range from 1-5 μm to greater than 12 μm. The fluorides, the low index constituents in the mixtures, have very low water solubility compared to the other commonly used alkali earth fluorides and are chemically very stable. SrF_2 and ZnSe have crystalline structures with cubic symmetry and lattice constants differing by about 2%, whereas Si and YF_3 have different crystalline symmetries and lattice constants. This enabled a study of the effect of similar and dissimilar lattice structures on mixed film properties.

Experimental

Mixed composition thin films were deposited by coevaporation from separate sources. Si was evaporated in an electron beam source and ZnSe and YF_3 were evaporated from resistively heated crucibles. SrF_2 was evaporated using a cw CO_2 laser. Composition was controlled using crystal monitors during the deposition and was analyzed by energy dispersive X-ray analysis after the deposition. With a few exceptions,the substrate temperature was 200°C and the background pressure during deposition was 2×10^{-7} Torr.

Various substrate materials and film thicknesses were used depending on the analysis techniques. Films, 2-4 microns thick, were grown on Si and GaAs wafers for structural and optical scatter studies. Stress was measured in 2-4 micron thick films deposited on thin glass plates by the cantilevered beam technique using a special beam holder.[5] Films, 1500Å thick, were deposited on NaCl substrates for TEM analysis.

Crystallinity was measured by x-ray diffraction and by TEM. The films were subjected to post deposition anneal in nitrogen at various temperatures up to 550°C for 16 hr. Their crystallinity was characterized and compared to the as-deposited values.

Refractive index was measured by ellipsometry. A qualitative measure of optical scattering was obtained by measuring the light scattered at 40 degrees from normal with a white light source incident normal to the film surface. Absorbed water content in the films was measured by infrared spectroscopy.

Results and Discussion

To emphasize the structure-property relationships the structural data will be presented first followed by optical and stress data.

$ZnSe-SrF_2$ System: X-ray diffraction studies indicated that films of all compositions were crystalline and oriented. The intermediate compositions exhibited both SrF_2 and ZnSe crystalline phases, albeit one or the other was dominant. This indicates that mixing does not occur on an atomic level in this system. Pure SrF_2 and SrF_2 rich films, with up to 70 molar % SrF_2, had 220 orientation of the SrF_2 cubic phase. The grains were large and oriented, as shown in Fig 1b. SrF_2 was also the dominant crystalline phase in films with compositions in the range 30 to 40% SrF_2, or 30 to 60% ZnSe, but with a different orientation, 200, and with smaller grains (Fig 1a). Thus higher concentrations of ZnSe induce a

change in the dominant orientation of SrF_2 probably due to changes in the surface energy of SrF_2 crystallites in the mixed composition environment. Films with greater than 60% ZnSe exhibited ZnSe 111 cubic phase, with grain size increasing with decreasing SrF_2 content. The composition ranges where the above orientations dominate are indicated in Fig 3.

The morphology of the pure SrF_2 films was rough with jagged columnar grains, as shown in Fig 2a. Addition of ZnSe reduced the roughness monotonically until the composition reached 30% ZnSe, where the SrF_2 orientation changes from 220 to 200 (Fig 2b). Films with 30% and greater concentrations of ZnSe had smooth morphologies, typical of pure ZnSe.

The effect of composition on optical scatter is shown in Fig 3. The scattered radiation in SrF_2 rich films decreases with the addition of ZnSe and in films with 30% ZnSe reaches a value about a factor of 10 less than that in pure SrF_2 films. This low scatter is characteristic of all films having 30 - 100% ZnSe. Low scatter and smooth morphology prevail not only in ZnSe rich films, but also in mixed composition films where SrF_2 crystallinity dominates with 200 orientation (up to 70% SrF_2) but not in mixed composition films with 220 SrF_2 orientation. The scatter in pure SrF_2 films was 2.15%.

One micron thick films of the pure constituents were observed to grow epitaxially when deposited upon each other (i.e. ZnSe over SrF_2 and vice versa). These films had rough morphologies, due to the SrF_2 layers, with ZnSe causing a slight smoothing when it was deposited over SrF_2. This indicates that multilayered coatings of ZnSe and SrF_2 will have rough morphology. The limit of very thin layers (e.g., 200Å), where the rough morphology of SrF_2 might not be fully developed, was not investigated.

The stress properties of these films are shown in Fig 4. The compressive stress characteristic of ZnSe persists unaltered for compositions up to 70% SrF_2. Stress remains

compressive for compositions richer in SrF_2, but decreases with SrF_2 content, achieving a very low value for pure SrF_2 films. Low intrinsic stress values in thick (i.e., > 1 micron) films have been observed in other evaporated dielectrics.[6] Therefore the stress in thin (i.e., < 1 micron) pure SrF_2 is thought to be greater than that in thick films, (and tensile) in analogy with other alkali earth fluoride thin films.

Optical scatter and mechanical stress both exhibit an abrupt transition at 70% SrF_2. Structural properties of the mixed composition films also change abruptly becoming more "SrF_2-like" for 70% and higher SrF_2 content.

Mixed composition films deposited on 200°C substrates were more crystalline than films deposited on ambient temperature substrates that were subsequently annealed at 200°C for 16 hours. Similarly, annealing the films deposited on 200°C substrates at temperatures of 300, 400, 500°C induced virtually no change in crystallinity, grain size and orientation of SrF_2 and ZnSe crystallites. These results suggest that bulk diffusion does not play a role in phase separation in this system and that the coexistence of different phases in the as-deposited films is due to surface segregation during deposition. Increasing the rate of deposition resulted in reduced crystallinity, a result that also supports the above picture, since the time available for surface diffusion will decrease at higher deposition rates.

The refractive index of the mixed films varied linearly with composition. The scatter in the data, mainly due to uncertainties in the composition (~ 5%), was large enough to mask small nonlinearities. Therefore no attempt was made to fit the data to any model of dielectric mixtures.

$\underline{Si-YF_3}$ - Mixed composition $Si-YF_3$ films that were deposited on 200°C substrates were amorphous for compositions of 20-100% Si. Pure YF_3, and YF_3-rich films with compositions up to about 20% Si, were crystalline (orthorombic) with 011 orientation.

Annealing at 400°C induced phase separation and crystallinity in films with up to 40% Si, and a 550°C anneal brought out crystallinity in films with up to 70% Si. Films with higher Si content remained amorphous at 550°C. The temperature for crystallization of films having higher than 70% Si could not be established because higher temperature anneals caused extensive cracking and peeling of the films.

The morphology of the pure YF_3 films was qualitatively rougher than that of the pure SrF_2 films (Fig 5a). Addition of 20% or more Si, which in its pure form grows with featureless morphology, smoothed out the morphology of the mixed composition films (Fig. 5b), as did the addition of ZnSe to SrF_2-rich films. SEM analysis indicated that annealing and crystallization did not affect the morphology of the mixed composition films.

Pure YF_3 films exhibited absorption at 3400 cm^{-1}, indicative of absorbed water. Addition of Si reduced the amount of absorbed water in the films and no water absorption was observed in films having 20% or higher concentrations of Si.

The intrinsic stress properties of Si-YF_3 films are shown in Fig 6. Both YF_3 and Si have high tensile stress. Mixing reduces this stress and for the intermediate compositions of 40 - 60% causes it to be slightly compressive. Obviously these compositions are desirable for the deposition of thick films to avoid stress-induced mechanical failure. This stress-composition behavior is reminiscent of that observed in Ge mixtures with MgF_2 and CeF_3.[4]

The origin of the tensile stress in the pure component films is probably the attractive forces at the boundaries of Si or YF_3 grains. Mixed composition films, on the other hand, could have Si rich and YF_3 rich grains, assuming small scale segregation during deposition due to the immiscibility in this system. In the middle of the compositional range the number of boundaries between Si and YF_3 rich grains will be maximum. The observed stress characteristics could be explained if weakly attractive or repulsive forces between

50

unlike grains are assumed, which will result in a weakly tensile or compressive net force, respectively.

Conclusion

Two binary material systems were studied for potential mixed composition infrared thin film applications. $ZnSe$-SrF_2 mixtures exhibited different behaviours in two compositional regions with 70% SrF_2 being roughly the dividing line. ZnSe rich films have high compressive stress but smooth morphology whereas SrF_2 rich films have low stress but rough morphology and high optical scatter. Si-YF_3 films with intermediate compositions exhibited very low compressive stress, smooth morphology and noncrystalline structure. These films did not exhibit infrared water absorption bands and were also stable with respect to crystallization for annealing temperatures up to 400°C. These results indicate that the Si-YF_3 is the more desirable system for thick film applications.
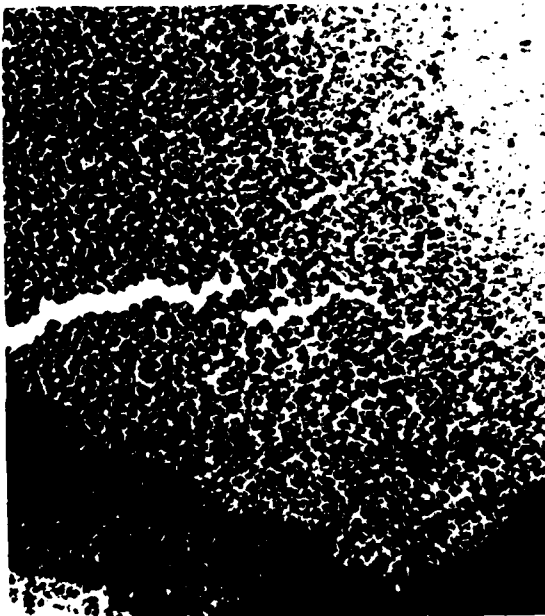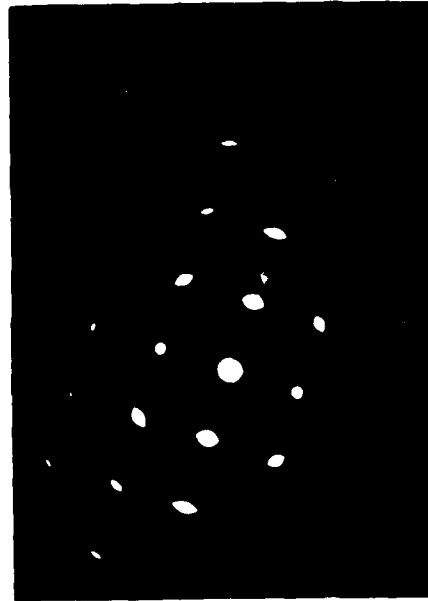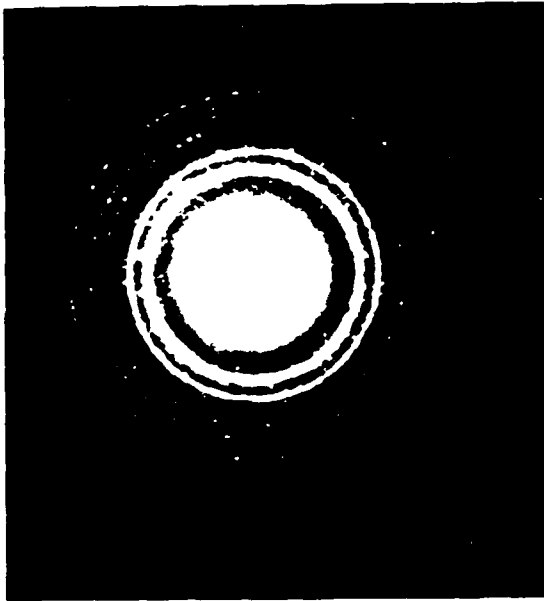
Acknowledgement

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Figure captions

Fig. 1   TEM micrographs and selected area diffraction patterns of (a) intermediate (60% SrF_2) composition films, and (b) SrF_2 rich (82% SrF_2) films.

Fig. 2   SEM micrographs showing the surface morphology of thin films a) 80% SrF_2, b) 70% SrF_2, and c) 60% SrF_2.

Fig. 3   Optical scatter vs film composition in SrF_2-ZnSe system.

Fig. 4   Intrinsic stress vs film composition in SrF_2-ZnSe system.

Fig. 5   Surface morphology of thin films of a) YF_3 and b) 20% Si-80% YF_3.

Fig. 6   Intrinsic stress vs composition in YF_3-Si system.
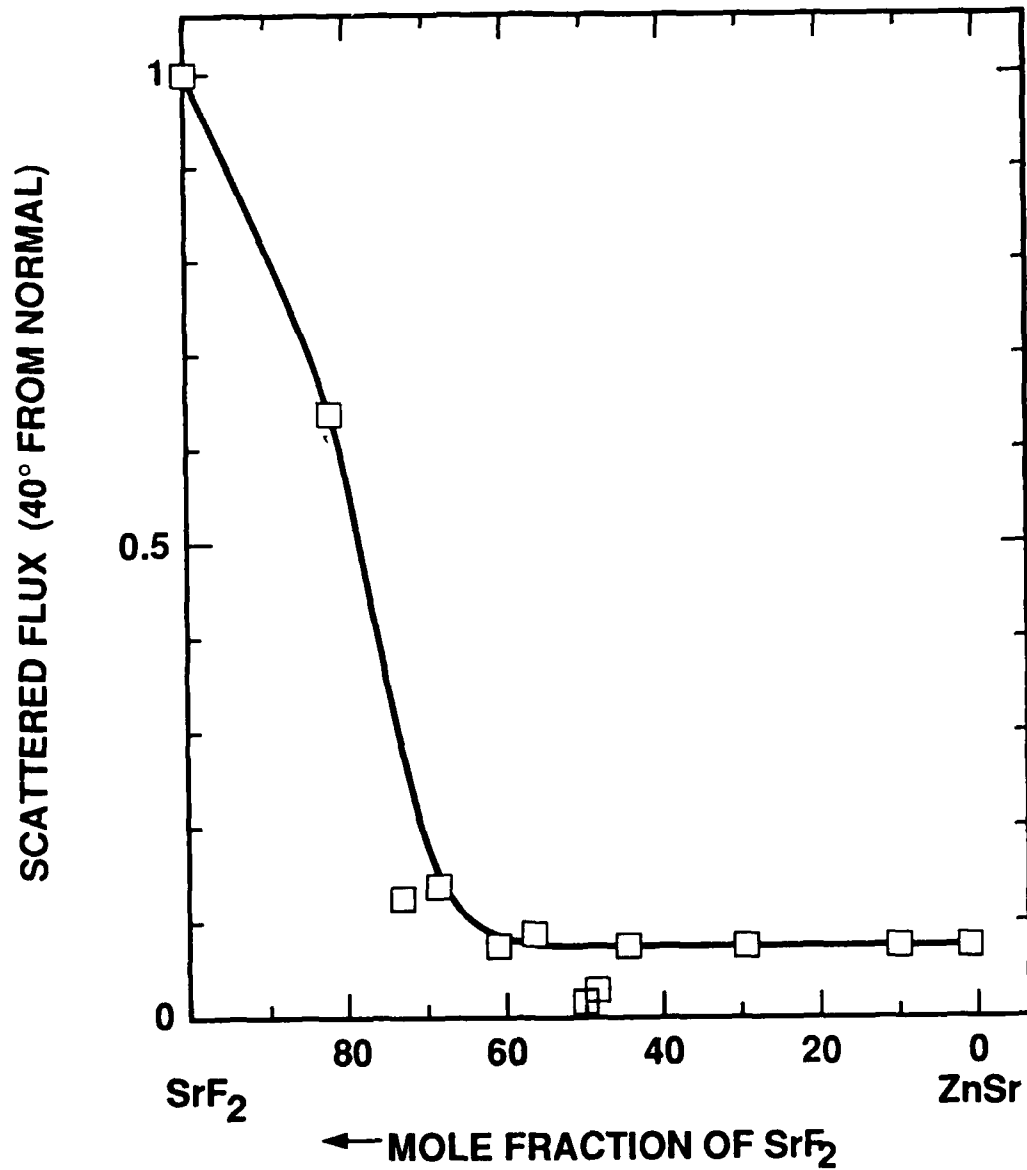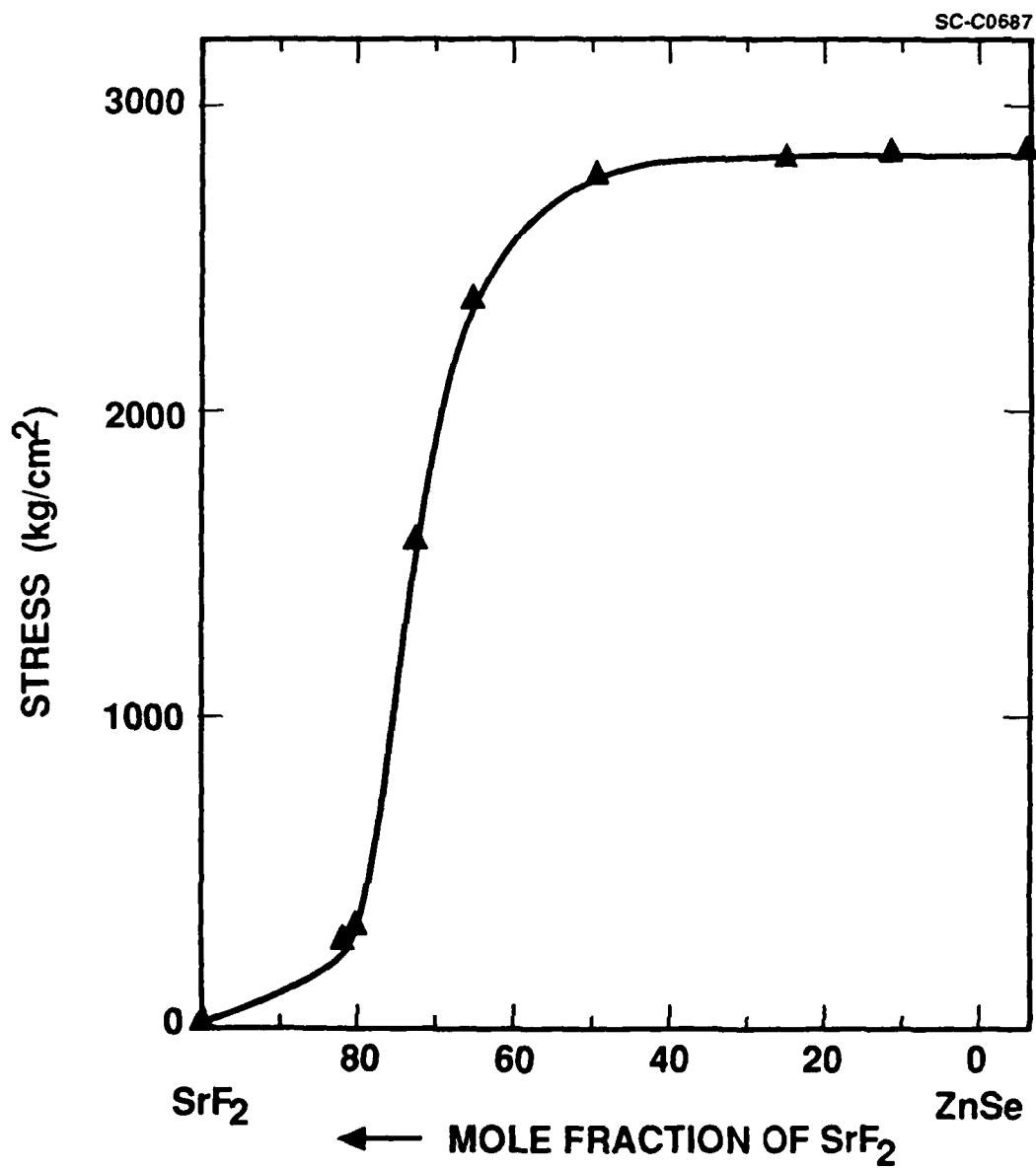
(a)　　　　　　　1 μm

(b)　　1 μm

54

(a)

(b)

(c)
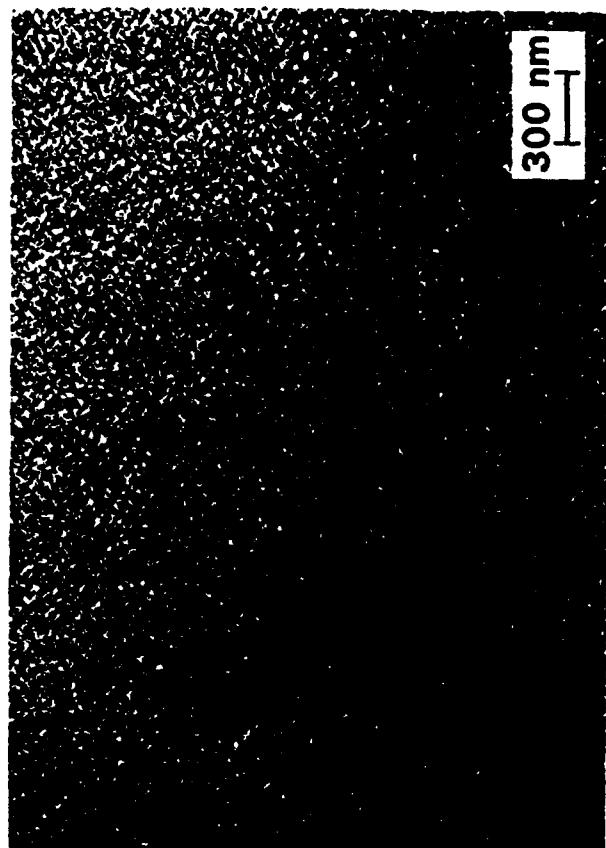
├───────┤
1 μm

SCATTERED FLUX (40° FROM NORMAL)

MOLE FRACTION OF SrF$_2$

SrF$_2$

ZnSr

220 SrF$_2$

200 SrF$_2$

111 ZnSe

SC-C0687

57

SC50682

(b)

300 nm

(a)

300 nm

58

SC-C0686

COMPRESSIVE

TENSILE

MOLE FRACTION OF Si

STRESS (kg/cm^2)

YF$_3$

Si